

# ATOMIC SPECTRAL METHODS FOR MOLECULAR ELECTRONIC STRUCTURE CALCULATIONS<sup>†</sup>

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**Abstract.** New theoretical methods are reported for *ab initio* calculations of the adiabatic (Born-Oppenheimer) electronic wave functions and potential energy surfaces of molecules and other atomic aggregates. An outer product of complete sets of atomic eigenstates familiar from perturbation-theoretical treatments of long-range interactions is employed as a representational basis without prior enforcement of aggregate wave function antisymmetry. The nature and attributes of this atomic spectral-product basis are indicated, completeness proofs for representation of antisymmetric states provided, convergence of Schrödinger eigenstates in the basis established, and strategies for computational implementation of the theory described. A diabatic-like Hamiltonian matrix representative is obtained which is additive in atomic-energy and pairwise-atomic interaction-energy matrices, providing a basis for molecular calculations in terms of the (Coulombic) interactions of the atomic constituents. The spectral-product basis is shown to contain the totally antisymmetric irreducible representation of the symmetric group of aggregate electron coordinate permutations once and only once, but to also span other (non-Pauli) symmetric group representations known to contain unphysical discrete states and associated continua in which the physically significant Schrödinger eigenstates are generally embedded. These unphysical representations are avoided by isolating the physical block of the Hamiltonian matrix with a unitary transformation obtained from the metric matrix of the explicitly antisymmetrized spectral-product basis. A formal proof of convergence is given in the limit of spectral closure to wave functions and energy surfaces obtained employing conventional prior antisymmetrization, but determined without repeated calculations of Hamiltonian matrix elements as integrals over explicitly antisymmetric aggregate basis states. Computational implementations of the theory employ efficient recursive methods which avoid explicit construction the metric matrix and do not require storage of the full Hamiltonian matrix to isolate the antisymmetric subspace of the spectral-product representation. Calculations of the lowest-lying singlet and triplet electronic states of the covalent electron pair bond ( $\text{H}_2$ ) illustrate the various theorems devised and demonstrate the degree of convergence achieved to values obtained employing conventional prior antisymmetrization. Concluding remarks place the atomic spectral-product development in the context of currently employed approaches for *ab initio* construction of adiabatic electronic eigenfunctions and potential energy surfaces, provide comparisons with earlier related approaches, and indicate prospects for more general applications of the method.

## 1.0 Introduction

Adiabatic electronic wave functions provide well-known first approximations to the physical attributes of molecules and other forms of matter,<sup>1–3</sup> and are prerequisites for studies of the non-adiabatic dynamical consequences of avoided crossings and conical intersections in the potential energy surfaces that guide the pathways of chemical reactions.<sup>4–6</sup> Methods currently employed for constructing such wave functions and energy surfaces include *ab initio* quantum chemistry,<sup>7–10</sup> quantum Monte-Carlo simulations,<sup>11,12</sup> density-functional approaches,<sup>13–18</sup> semi-empirical techniques,<sup>19–23</sup> hybrid quantum mechanical/molecular mechanical (QM/MM) combinations,<sup>24</sup> and various forms of long-range perturbation theory.<sup>25–38</sup> Although these methods have provided a significant amount of useful information over the past few decades, they arguably do not constitute a quantum theory of chemical bonding, which would preferably express the chemical attributes of compounds in terms of intrinsic properties of their atomic constituents. New approaches in this spirit to construction of adiabatic electronic wave functions are clearly welcome, particularly if they can retain the desirable features of the existing methods while ameliorating some of their shortcomings.

The *ab initio* approaches employing multi-configurational Hartree-Fock, Møller-Plessett perturbation theory, and multi-reference configuration mixing methods,<sup>7,8</sup> and the coupled-cluster,<sup>9</sup> valence-bond,<sup>10</sup> and quantum Monte Carlo<sup>11,12</sup> approaches, can provide highly accurate energies and other properties for the ground and excited states of small molecules, but they generally require allocations of significant computational resources for this purpose, and they are apparently not yet applicable to large atomic aggregates. By contrast, the widely employed density-functional,<sup>13–18</sup> semi-empirical,<sup>19–23</sup> and QM/MM<sup>24</sup> approaches can be applied to larger aggregates, including atomic clusters,<sup>22</sup> condensed matter systems,<sup>23</sup> and biological macromolecules,<sup>24</sup> and in certain cases provide electronically excited states, although their *a priori* accuracy is frequently unknown. Long-range Rayleigh-Schrödinger and symmetry-adapted perturbation theories have also proved useful in appropriate limits,<sup>25–38</sup> although widespread and systematic applications of perturbation theory to chemical interactions are apparently not yet in evidence. These methods have all contributed to the collective development of a significant methodological and computational base from which to draw upon in devising new *ab initio* approaches to electronic-structure and spectral calculations.<sup>39–44</sup>

In the present manuscript, new theoretical methods are described for *ab initio* calculations of the adiabatic electronic wave functions and potential energy surfaces of molecules and other atomic aggregates.<sup>45</sup> Certain of the desirable attributes of the computational methods currently in play for these purposes are incorporated in the development, which employs an outer product of complete sets of atomic spectral eigenfunctions familiar from the aforementioned perturbation-theoretical treatments of long-range atomic interactions.<sup>25</sup> In contrast to related earlier developments which employ *prior* antisymmetrization of products of atomic wave functions in atoms-in-molecules approaches,<sup>46–58</sup> antisymmetry is enforced in the present development *subsequent* to construction of the Hamiltonian matrix employing a unitary transformation to isolate its antisymmetric subspace. The total electronic Hamiltonian operator in the atomic-product representation takes a matrix form in which the individual atomic energies appear explicitly as constants independent

of atomic positions, with only a sum of pairwise-atomic interaction-energy matrices requiring repeated evaluation as a function of aggregate atomic configuration in potential-energy-surface calculations. The pairwise interaction-energy matrices depend only upon the vector separations of the two interacting atoms, are independent of the positions of all other atoms in the aggregate, and can be expressed in terms of one-electron *atomic* charge and transition densities, which provide the computational invariants of the development. Accordingly, the present approach does not require repeated calculations of Hamiltonian matrix elements as integrals over antisymmetric many-electron aggregate basis functions; rather, one-electron atomic charge and transition densities are calculated once and for all for a spectrum of atomic states and retained for repeated use in construction of the Hamiltonian matrix for arbitrary spatial arrangements of interacting atoms.

Notational conventions are established and the (Coulombic) form of the many-electron Hamiltonian operator employed in the development given in Section 2. The atomic spectral-product basis and certain of its attributes are described in Section 3 employing complete sets of spin orbitals in representations of the many-electron atomic spectral eigenstates. It is shown that the totally antisymmetric irreducible representation of the aggregate symmetric group is spanned once and only once by the atomic-product basis, although other (non-Pauli) symmetric-group representations are also contained in the reducible product. The form of the Hamiltonian matrix in the spectral-product representation is given in Section 4, methods are described for its evaluation in terms of one-electron atomic transition-density matrices, and certain attributes of the spectrum of the Hamiltonian matrix are indicated. In Section 5, methods are reported for formal isolation of the totally antisymmetric block of the spectral-product Hamiltonian matrix employing a unitary transformation derived from the metric matrix of the antisymmetrized spectral-product basis. Convergence is demonstrated in this way to eigenstates and energies identical to those obtained in the linearly independent subspace of this prior antisymmetrized representation. Aspects of the theory are illustrated with calculations reported in Section 6, which employ efficient recursive methods for isolating the totally antisymmetric block of the Hamiltonian matrix, avoiding explicit construction of the metric matrix and of the entire Hamiltonian matrix at any one time. Convergence to the lowest-lying singlet and triplet potential energy curves of the electron pair bond ( $\text{H}_2$ ) is achieved employing even-tempered Gaussian orbital representations and related computational methodology. Finally, the new development is discussed in the context of currently employed electronic-structure approaches, comparisons are made with related earlier theoretical methods, and prospects for more general applications of the method are indicated in concluding remarks provided in Section 7.

## 2.0 The Aggregate Schrödinger Equation

The adiabatic electronic eigenstates and energies of an  $N$ -atom molecule or other atomic aggregate are obtained from the Schrödinger equation

$$\hat{H}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) \Psi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) = \Psi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) \cdot \mathbf{E}(\mathbf{R}), \quad (1)$$

where  $\Psi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R})$  is a row vector of orthonormal eigenstates  $\Psi_\Gamma(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R})$  having quantum labels  $\Gamma$  and  $\mathbf{E}(\mathbf{R})$  is the diagonal matrix of corresponding eigenvalues

$E_T(\mathbf{R})$ . The Hamiltonian operator appearing in Eq. (1) is written in the form

$$\hat{H}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) = \sum_{\alpha=1}^N \left\{ \hat{H}^{(\alpha)}(\mathbf{i} : \mathbf{R}_{\alpha}) + \sum_{\beta=\alpha+1}^N \hat{V}^{(\alpha,\beta)}(\mathbf{i}; \mathbf{j} : \mathbf{R}_{\alpha\beta}) \right\}, \quad (2)$$

where

$$\hat{H}^{(\alpha)}(\mathbf{i} : \mathbf{R}_{\alpha}) = \sum_i^{n_{\alpha}} \left\{ -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Z_{\alpha} e^2}{r_{i\alpha}} + \sum_{i'=i+1}^{n_{\alpha}} \frac{e^2}{r_{ii'}} \right\} \quad (3)$$

is the Hamiltonian operator in the familiar Coulomb approximation for a set of  $n_{\alpha}$  electrons which are arbitrarily associated with the atomic nucleus at position  $\mathbf{R}_{\alpha}$ , and whose  $3n_{\alpha}$  spatial coordinates are represented by the single vector label  $\mathbf{i}$ , and

$$\hat{V}^{(\alpha,\beta)}(\mathbf{i}; \mathbf{j} : \mathbf{R}_{\alpha\beta}) = \frac{Z_{\alpha} Z_{\beta} e^2}{R_{\alpha\beta}} - \sum_i^{n_{\alpha}} \frac{Z_{\beta} e^2}{r_{i\beta}} - \sum_j^{n_{\beta}} \frac{Z_{\alpha} e^2}{r_{j\alpha}} + \sum_i^{n_{\alpha}} \sum_j^{n_{\beta}} \frac{e^2}{r_{ij}} \quad (4)$$

is the Coulombic interaction potential between atoms  $\alpha$  and  $\beta$ , where the coordinate label  $\mathbf{j}$  refers to the  $3n_{\beta}$  spatial electron coordinates arbitrarily associated with the atomic nucleus at the position  $\mathbf{R}_{\beta}$ .<sup>59</sup> The indices  $\mathbf{1}, \mathbf{2}, \dots, \mathbf{n}$  in Eqs. (1) and (2) represent the collected spatial coordinates of disjoint sets of electrons, each arbitrarily associated with one of the atomic nuclei in the aggregate.

In the foregoing equations and throughout the development, all electron ( $\mathbf{r}_i$ ) and atomic-position ( $\mathbf{R}_{\alpha}$ ) coordinates are defined in the laboratory frame,  $\mathbf{r}_{i\alpha} = \mathbf{r}_i - \mathbf{R}_{\alpha}$  and  $\mathbf{r}_{j\beta} = \mathbf{r}_j - \mathbf{R}_{\beta}$  are electron coordinate vectors relative to the indicated atomic positions,  $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$  is the  $(i, j)$  electron vector separation,  $\mathbf{R}_{\alpha\beta} = \mathbf{R}_{\alpha} - \mathbf{R}_{\beta}$  is the  $(\alpha, \beta)$  atomic position vector separation,  $\mathbf{R} = (\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N)$  specifies the positions of all the atoms in the entire aggregate,  $e$  is the magnitude of the electronic charge,  $m$  is the electron mass,  $Z_{\alpha}$  and  $Z_{\beta}$  are atomic numbers, and the other symbols have their usual meanings.<sup>59</sup> A colon is employed to separate electron coordinates from atomic positions ( $\mathbf{i} : \mathbf{R}_{\alpha}$ ), and a semi-colon is employed in Eq. (4) to distinguish sets of electrons ( $\mathbf{i}; \mathbf{j}$ ) between which the interaction potential  $\hat{V}^{(\alpha,\beta)}(\mathbf{i}; \mathbf{j} : \mathbf{R}_{\alpha\beta})$  is not totally symmetric under coordinate permutations. Of course, the  $n_t$ -electron ( $n_t = n_1 + n_2 + \dots + n_N$ ) aggregate Hamiltonian  $\hat{H}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R})$  and the individual  $n_{\alpha}$ -electron atomic Hamiltonians  $\hat{H}^{(\alpha)}(\mathbf{i} : \mathbf{R}_{\alpha})$  are symmetric sums of one- and two-electron operators in their respective electron labels. Accordingly, the notation employed in Eqs. (1) to (4) does not by itself constitute a meaningful assignment of particular electrons to particular atoms, although it does suggest this possibility in conjunction with the choice of an appropriate electronic representational basis.

The physical eigenstates  $\Psi^{(p)}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R})$  and eigenvalues  $\mathbf{E}^{(p)}(\mathbf{R})$  included in the solutions of Eq. (1) for the Hamiltonian of Eqs. (2) to (4) have good total spin and spin-projection quantum numbers ( $S, M_S$ ) and transform as the totally antisymmetric representation ( $1^{n_t}$ ) of the symmetric group  $S_{n_t}$  of the aggregate electron spin and spatial coordinate permutations,<sup>60</sup> whereas additional (non-Pauli) eigensolutions  $\Psi^{(u)}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R})$

of Eq. (1) which transform as other than the totally antisymmetric irreducible representation under electron coordinate permutations are generally regarded as unphysical, as are the corresponding energies  $\mathbf{E}^{(u)}(\mathbf{R})$ .<sup>61</sup>

### 3.0 Definition and Attributes of the Spectral-Product Basis

The physical and unphysical solutions of Eq. (1) which together comprise the full spectrum of the Hamiltonian operator of Eqs. (2) to (4) can be constructed in a many-electron spectral-product basis the nature and attributes of which are described in this section. The presence of unphysical states and the importance of devising methods for their elimination is emphasized throughout the development.

### 3.1 Spin-Orbital Basis Sets

Conventional variational approximations to the solutions of Eq. (1) in their most common form employ one-electron basis sets of atomic spin orbitals in Slater, Gaussian, or other forms centered at each of the aggregate atoms ( $\alpha = 1, 2, \dots, N$ ). Such basis sets, employed here largely for purposes of analysis,<sup>62</sup> are conveniently written as row vectors  $\phi^{(\alpha)}(i : \mathbf{R}_\alpha)$  of orthonormal one-electron functions  $\phi_{\gamma_\alpha}^{(\alpha)}(i : \mathbf{R}_\alpha)$  of the individual electronic spin and of spatial coordinates measured relative to the atomic positions ( $i \equiv \mathbf{r}_i - \mathbf{R}_\alpha$ ). These functions are generally enumerated employing an appropriate set of quantum labels  $\gamma_\alpha$ , are assumed complete in a finite three-dimensional spatial domain, and, accordingly, satisfy the closure relation

$$\phi^{(\alpha)}(i : \mathbf{R}_\alpha) \cdot \phi^{(\alpha)}(i' : \mathbf{R}_\alpha)^\dagger \equiv \sum_{\gamma_\alpha=1}^{\infty} \phi_{\gamma_\alpha}^{(\alpha)}(i : \mathbf{R}_\alpha) \phi_{\gamma_\alpha}^{(\alpha)}(i' : \mathbf{R}_\alpha)^* \rightarrow \delta^{(\alpha)}(i - i') \quad (5)$$

in this domain, where  $\phi^{(\alpha)}(i' : \mathbf{R}_\alpha)^\dagger$  is a column vector comprised of the complex conjugate spin orbitals  $\phi_{\gamma_\alpha}^{(\alpha)}(i' : \mathbf{R}_\alpha)^*$ . The choice of particular spin orbitals employed in Eq. (5) is arbitrary in the limit of a complete set, but the rate of convergence of computational developments built upon them will generally depend upon the specific basis employed.<sup>62</sup>

Traditional uses of these one-electron basis sets in connection with solution of Eq. (1) follow well-known molecular-orbital or valence-bond methods in constructing many-electron representational basis sets.<sup>63</sup> These conventional developments have in common the representation of each electron in a “symmetrical” or “democratic” manner and the use of prior term-by-term electron coordinate antisymmetrization of the many-electron basis employed.<sup>61</sup> In the molecular-orbital approaches, the common one-electron basis set that extends over the  $3n_t$ -dimensional spatial domain of the aggregate is employed to describe the positions of any of the electrons in antisymmetric Slater determinants,<sup>7,8</sup> whereas in the valence-bond methods over-all term-by-term prior antisymmetry insures the canonical spin-paired product states employed treat the electrons in a democratic fashion.<sup>10</sup> Of course, use of prior antisymmetry, and of symmetry adaptation more generally, guarantees that the matrix representative of the Hamiltonian operator obtained will be block diagonal and of minimal possible dimension for the states of interest in the basis employed, in accordance with Schur’s lemmas.<sup>60</sup>

### 3.2 Many-Electron Outer-Product Basis Set

In contrast to the aforementioned conventional developments, it is possible to forego prior symmetry adaptation of the individual terms in the many-electron basis set in favor of other potential advantages and simplifications by employing  $n_t$ -electron states which are not individually antisymmetric at the outset. Such states can be constructed from products of  $n_\alpha$ -electron atomic basis states which themselves are written in the form of simple products of spin orbitals,

$$\Pi_{\Gamma_\alpha}^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha) = \prod_{\gamma_\alpha}^{n_\alpha} \phi_{\gamma_\alpha}^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha), \quad (6)$$

where the label  $\Gamma_\alpha$  specifies a particular choice of spin orbitals on the atom  $\alpha$  in the indicated  $n_\alpha$ -term product. The row vector  $\Pi^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha)$  obtained from all  $\Gamma_\alpha$  values includes all possible unrestricted spin-orbital products in Eq. (6), thereby providing a complete representational basis for  $n_\alpha$ -electron eigenstates consequent of Eq. (5). Accordingly, the complete outer product of such states for all atoms in the aggregate, written in the form of the complete separable Hilbert space

$$\Pi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) = \left\{ \Pi^{(1)}(\mathbf{1} : \mathbf{R}_1) \otimes \Pi^{(2)}(\mathbf{2} : \mathbf{R}_2) \otimes \dots \Pi^{(N)}(\mathbf{n} : \mathbf{R}_N) \right\}_O, \quad (7)$$

similarly provides a complete representational basis for the entire  $n_t$ -electron aggregate. Here, semi-colons are employed to separate groups of electrons  $(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n})$  distinguished by virtue of their representations in the *different* sets of spin-orbital product states employed for each atom, whereas the outer-product symbol " $\otimes$ " is used to indicate that all possible products of the atomic basis functions are included in the vector  $\Pi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R})$ . The bracket symbol  $\{\dots\}_O$  implies choice of a particular rule for enumerating and ordering the product functions in the row vector  $\Pi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R})$ , which rule, although arbitrary, must be adhered to in matrices constructed in the outer-product basis and in related vector and matrix multiplications.

The basis of Eq. (7), in which specific sets of electrons  $(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n})$  are arbitrarily assigned to specific atoms  $(1, 2, \dots, N)$  and are described employing different sets of orbital functions [Eq. (5)], does not provide individual  $n_t$ -electron functions which transform irreducibly under aggregate electron coordinate permutations, nor are these functions generally eigenstates of total electron spin or of other aggregate commuting operators. Nevertheless, as a consequence of the closure relations of Eq. (5) for the different sets of spin orbitals, the aggregate outer-product basis satisfies the closure relation

$$\Pi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) \cdot \Pi(\mathbf{1}'; \mathbf{2}'; \dots; \mathbf{n}' : \mathbf{R})^\dagger = \prod_{\alpha=1}^N \Pi^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha) \cdot \Pi^{(\alpha)}(\mathbf{i}' : \mathbf{R}_\alpha)^\dagger \rightarrow \prod_{\alpha=1}^N \delta^{(\alpha)}(\mathbf{i} - \mathbf{i}'), \quad (8)$$

where the product of delta functions on the right-hand side expresses completeness of the basis as a separable Hilbert space in the spin coordinates and over a  $3n_t$ -dimensional spatial domain. Accordingly, convergence at least in the norm to physical and unphysical eigenstates of irreducible symmetry can be achieved in the basis of Eqs. (5) to (8), potentially providing approximations to any of the aggregate Schrödinger eigensolutions of Eq. (1).



### 3.3 Atomic Spectral Eigenstates

It is convenient to perform a series of formal unitary transformations of the complete product basis sets of Eq. (6) which bring the matrix representatives of the individual atomic Hamiltonian operators of Eq. (3) into diagonal forms, thereby simplifying the total Hamiltonian matrix but leaving the solutions of Eq. (1) in the basis invariant. Specifically, because a single spin-orbital basis set is used for all electrons  $\mathbf{i}$  on atom  $\alpha$ , and all spin-orbital products are present in Eq. (6), all permutations among electron coordinates  $\mathbf{i}$  are also included explicitly for each atomic site. It should be recalled in this connection that all permutations of electron coordinates among the spin-orbital products of Eq. (6) are included explicitly in conventional atomic structure theory, so that the orbital configurations employed to represent atomic states must be limited to sets of *ordered* spin-orbital products in Slater determinants to insure the linear independence of the basis states employed.<sup>62</sup> The present development, in which all orderings of spin-orbital products for a given atom are included but only a single assignment of electrons to spin orbitals is made, is entirely equivalent to the standard method because a common spin-orbital basis is employed in a symmetrical representation of all the electrons in a given atom.<sup>61</sup>

The eigenstates of the atomic Hamiltonian of Eq. (3),

$$\hat{H}^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha) \Phi^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha) = \Phi^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha) \cdot \mathbf{E}^{(\alpha)}, \quad (9)$$

are represented in the form

$$\Phi^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha) = \Pi^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha) \cdot \mathbf{U}^{(\alpha)}, \quad (10)$$

where the unitary transformation matrix  $\mathbf{U}^{(\alpha)}$  is independent of  $\mathbf{R}_\alpha$ , and  $\mathbf{E}^{(\alpha)}$  is the diagonal matrix of all atomic eigenvalues of the atom  $\alpha$  obtained from the matrix Schrödinger equation

$$\langle \Pi^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha) | \hat{H}^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha) | \Pi^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha) \rangle \cdot \mathbf{U}^{(\alpha)} = \mathbf{U}^{(\alpha)} \cdot \mathbf{E}^{(\alpha)}. \quad (11)$$

In Eq. (11), an outer-vector-product convention is employed on the left-hand side to provide matrices having conventional row and column labels formed from the indicated bra  $\langle \Pi^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha) |$  and ket  $| \Pi^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha) \rangle$  vectors. The irreducible-symmetry labels or good quantum numbers of the eigenstates of Eq. (9) can also be accommodated into the transformation matrix of Eqs. (10) and (11) without loss of generality, and so  $\Phi^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha)$  can be taken to be a row vector of functions  $\Phi_{\Gamma_\alpha}^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha)$  which are multiplet eigenstates of the Hamiltonian  $\hat{H}^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha)$  having specific energy  $E_{\Gamma_\alpha}$ , orbital and spin angular momentum, and parity values; i.e.,  $\Gamma_\alpha \equiv (E, L, M_L, S, M_S, P)_\alpha$ .<sup>63</sup> These atomic eigenfunctions transform either as physical (totally antisymmetric) or unphysical (non-Pauli) irreducible representations under the coordinate permutation group  $S_{n_\alpha}$  for electrons in the set  $\mathbf{i}$ .<sup>60</sup>

Combining the unitary transformations of Eqs. (10) and (11) for all atoms in the aggregate, a complete set of products of atomic spectral eigenstates is obtained in the form

$$\Phi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) = \Pi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) \cdot \mathbf{U}, \quad (12)$$

where  $\mathbf{U} = \{\mathbf{U}^{(1)} \otimes \mathbf{U}^{(2)} \otimes \dots \mathbf{U}^{(N)}\}_O$  is the appropriately ordered outer matrix product of unitary transformation matrices of the individual spectral basis sets of Eqs. (10) and (11), and

$$\Phi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) = \left\{ \Phi^{(1)}(\mathbf{1} : \mathbf{R}_1) \otimes \Phi^{(2)}(\mathbf{2} : \mathbf{R}_2) \otimes \dots \Phi^{(N)}(\mathbf{n} : \mathbf{R}_N) \right\}_O \quad (13)$$

is the resulting complete set of ordered products of atomic spectral eigenstates. As a consequence of Eq. (8) and the definitions of Eqs. (9) to (12), the spectral-product states of Eq. (13) satisfy the closure relation

$$\Phi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) \cdot \Phi(\mathbf{1}'; \mathbf{2}'; \dots; \mathbf{n}' : \mathbf{R})^\dagger = \prod_{\alpha=1}^N \Phi^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha) \cdot \Phi^{(\alpha)}(\mathbf{i}' : \mathbf{R}_\alpha)^\dagger \rightarrow \prod_{\alpha=1}^N \delta^{(\alpha)}(\mathbf{i} - \mathbf{i}') \quad (14)$$

for all irreducible representations of  $S_{n_t}$ , and so can be employed in descriptions of any of the eigensolutions of Eq. (1). Use of the spectral-product representation of Eq. (13) in place of the outer-product representation of Eq. (7) constitutes a partial pre-diagonalization of the aggregate Hamiltonian matrix which leaves its dimension unchanged and otherwise provides results equivalent to those obtained from the outer-product basis.

### 3.4 Restriction to Antisymmetric Atomic States

In view of the non-symmetrical nature of the spectral-product basis of Eq. (13), and of the fact that the outer product of the symmetric groups of the individual atomic constituents forms a subgroup of the full electron-coordinate permutation group ( $S_1 \otimes S_2 \otimes \dots S_N \subset S_{n_t}$ ), some care must be exercised in employing standard group-theoretical procedures in identifying and isolating the desired totally antisymmetric representation ( $1^{n_t}$ ) of  $S_{n_t}$  contained in the basis. The appropriate group-theoretical product in this case is the outer product of subgroup representations, as opposed to the inner Kronecker group product which is commonly reduced employing a Clebsch-Gordan decomposition.<sup>60</sup> Moreover, in the representation of Eq. (13), although electron-coordinate permutations *within* each set  $\mathbf{i}$  are included *explicitly*, those permutations involving at least one transposition of electron coordinates from *different* sets  $\mathbf{i}$  and  $\mathbf{j}$  at the two atomic sites  $\alpha$  and  $\beta$  are spanned *implicitly*. Nevertheless, in the limit of the closure associated with use of all orderings of spin-orbital products in Eq. (13), the latter implicit electron coordinate permutations are all effectively present in Eq. (13) and the standard outer-product reduction theory applies.<sup>60</sup>

Although there is apparently no convenient way in which to use group-theoretical methods in the explicit construction of a particular irreducible subspace in the ordered-product representation of Eq. (13), the outer-product reduction procedure can, nevertheless, be employed as an analytical device in this connection.<sup>32</sup> In particular, it can be demonstrated that some (but not all) of the unwanted unphysical representations of  $S_{n_t}$  spanned by the basis of Eq. (13) are removed by the simple expedient of restricting the atomic eigenstates in the vectors  $\Phi^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha)$  for all atoms  $\alpha$  to the physical subspace “ $p$ ” of eigenstates  $\Phi_p^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha)$  which are antisymmetric in the  $n_\alpha$  electron coordinates  $\mathbf{i}$ . The required demonstration follows from the standard outer-product reduction rules,<sup>60</sup> which

indicate that the presence of any horizontal (“symmetric”) strip in either of two Young patterns associated with distinct symmetric groups disallows the appearance of the totally antisymmetric representation in the reduction of the outer-product of the two patterns in the combined permutation group. More specifically, the reduction of the outer product of any two irreducible representations  $(\gamma_n \otimes \gamma_m)$  of two distinct symmetric groups  $S_n, S_m$  into irreducible representations of the group  $S_{n+m}$  includes the totally antisymmetric representation  $1^{(n+m)}$  of  $S_{n+m}$  once and only once if and only if the two subgroup representations are the totally antisymmetric representations  $\gamma_n = 1^n$  and  $\gamma_m = 1^m$ . Letting  $S_n$  represent the symmetric group for the first  $\alpha - 1$  atoms in the aggregate ( $n = n_1 + n_2 + \dots n_{\alpha-1}$ ), setting  $S_m = S_{n_\alpha}$ , the symmetric group of the atom  $\alpha$ , and assuming that  $1^n$  is contained only once in  $S_n$ , it is seen that  $1^n \otimes \gamma_{n_\alpha}$  contains  $1^{(n+n_\alpha)}$  only once if and only if  $\gamma_{n_\alpha} = 1^{n_\alpha}$ . Correspondingly, it follows by induction that the totally antisymmetric representation  $1^{n_t}$  of  $S_{n_t}$  is obtained once and only once in the reduction of the entire outer product  $(\gamma_{n_1} \otimes \gamma_{n_2} \otimes \dots \gamma_{n_N})$  if and only if  $\gamma_{n_\alpha} = 1^{n_\alpha}$  for all  $\alpha$ .

In accordance with the foregoing observations, a complete but not over-complete linearly-independent orthonormal subspace of the spectral-product basis of Eq. (13) suitable for representations of totally antisymmetric aggregate states is contained in the products of the *physical* (antisymmetric) atomic eigenstates  $\Phi_p^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha)$ ,

$$\Phi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{N} : \mathbf{R}) = \left\{ \Phi_p^{(1)}(\mathbf{1} : \mathbf{R}_1) \otimes \Phi_p^{(2)}(\mathbf{2} : \mathbf{R}_2) \otimes \dots \Phi_p^{(N)}(\mathbf{n} : \mathbf{R}_N) \right\}_O. \quad (15)$$

The spectral closure relation of Eq. (14) correspondingly now becomes operative only in the subspace of irreducible representations of  $S_{n_t}$  spanned by the outer product of all antisymmetric atomic eigenstates,

$$\Phi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) \cdot \Phi(\mathbf{1}'; \mathbf{2}'; \dots; \mathbf{n}' : \mathbf{R})^\dagger = \prod_{\alpha=1}^N \Phi_p^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha) \cdot \Phi_p^{(\alpha)}(\mathbf{i}' : \mathbf{R}_\alpha)^\dagger \rightarrow \prod_{\alpha=1}^N \delta_p^{(\alpha)}(\mathbf{i} - \mathbf{i}'), \quad (16)$$

where  $\delta_p^{(\alpha)}(\mathbf{i} - \mathbf{i}')$  refers to the Dirac delta function in the totally antisymmetric physical subspace  $\Phi_p^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha)$  of the atomic states [cf., Eq. (14)].

Although some of the non-totally-antisymmetric representations of  $S_{n_t}$  present in the outer-product basis are generally absent in the basis of Eq. (15), a certain number of these non-Pauli representations are always present. The number and type of unphysical irreducible representations of  $S_{n_t}$  spanned by the reducible spectral-product representation of Eq. (15) is determined by the total number of electrons  $n_t$  and by the partitioning of these into the particular atomic values  $n_1, n_2, \dots, n_N$  employed. Although, strictly speaking, these unphysical irreducible representations are not explicitly required in the present development, they can be enumerated in specific cases employing the outer-product reduction rules in the usual way.<sup>60</sup> By this identification it is made clear that the basis of Eq. (15) can span unphysical states of very low energy arising from “over-filled” inner shells and their associated continua, in which the physical states can be embedded.<sup>32–37</sup>

The basis of Eq. (15) has been employed previously in a number of related connections, including long-range and exchange perturbation theories<sup>25–38</sup> and so-called atoms-in-molecules<sup>46–50</sup> and related diatomics-in-molecules<sup>51–58</sup> methods. In contrast to the

present development, the atoms-in-molecules approaches employ explicit prior antisymmetrization of the spectral-product basis of Eq. (15), in spite of the consequent linear dependence in the limit of closure this approach entails, and the perturbation-theoretical methods are generally applicable only in cases of weak long-range atomic interactions. The representation of Eq. (15) would appear to be particularly appropriate for molecules and other atomic aggregates even in the *absence* of prior aggregate antisymmetry in that it is strictly orthonormal and contains the antisymmetric representation only once, avoiding thereby problems of linear dependence. It furthermore isolates the most singular intra-atomic Coulombic interactions in the individual atomic wave functions employed as a basis, gives the exact aggregate energies in complete dissociation limits, and results in a Hamiltonian matrix of particularly simple form (see below). Additionally, the basis of Eq. (15) provides the possibility of developing an atomic-interaction-based approach for evaluating an aggregate eigenspectrum in which the exclusion principle among aggregate electrons is accommodated in accordance with the degree of interaction between atoms, rather than as a global constraint applied uniformly and uncritically among all electrons present, which constraint is generally not required in the case of highly separated or otherwise weakly-interacting atomic constituents.<sup>64</sup>

#### 4.0 Spectral-Product Representation of Schrödinger Eigenstates

The spectral-product basis defined in the preceding Section can be employed to construct solutions of Eq. (1) following standard variational procedures. Specifically, employing an expansion of eigenfunctions in the spectral-product basis of Eq. (15) in Eq. (1) and projecting with each of the orthonormal product functions in the basis in the usual way gives the familiar matrix Schrödinger equation<sup>63</sup>

$$\mathbf{H}(\mathbf{R}) \cdot \mathbf{U}_{\mathbf{H}}(\mathbf{R}) = \mathbf{U}_{\mathbf{H}}(\mathbf{R}) \cdot \mathbf{E}(\mathbf{R}), \quad (17)$$

where  $\mathbf{E}(\mathbf{R})$  is the desired diagonal matrix of aggregate eigenvalues, and the unitary matrix

$$\mathbf{U}_{\mathbf{H}}(\mathbf{R}) = \langle \Phi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) | \Psi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) \rangle \quad (18)$$

provides a representation of the Schrödinger eigenstates spanned by the basis of Eq. (15) in the form

$$\Psi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) = \Phi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) \cdot \mathbf{U}_{\mathbf{H}}(\mathbf{R}). \quad (19)$$

The semi-colons in the Schrödinger eigenstates  $\Psi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R})$  are employed to emphasize that these solutions are obtained from Eqs. (15) to (17), in which the orthonormal aggregate product-function basis states appearing in the expression of Eq. (19) for the wave functions are not individually antisymmetric under all electron-coordinate permutations.

#### 4.1 Form of the Hamiltonian Matrix

The matrix representative of the aggregate Hamiltonian operator appearing in Eq. (17) takes the form<sup>45</sup>

$$\mathbf{H}(\mathbf{R}) = \langle \Phi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) | \hat{H}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) | \Phi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) \rangle$$

$$= \sum_{\alpha=1}^N \left\{ \mathbf{H}^{(\alpha)} + \sum_{\beta=\alpha+1}^N \mathbf{V}^{(\alpha,\beta)}(\mathbf{R}_{\alpha\beta}) \right\}, \quad (20)$$

where  $\mathbf{H}^{(\alpha)}$  and  $\mathbf{V}^{(\alpha,\beta)}(\mathbf{R}_{\alpha\beta})$  are Hermitian matrix representatives of the operators of Eq. (3) and (4) in the spectral-product basis. The atomic energy matrix  $\mathbf{H}^{(\alpha)}$  is a constant diagonal matrix independent of atomic position vectors, whereas the interaction matrix  $\mathbf{V}^{(\alpha,\beta)}(\mathbf{R}_{\alpha\beta})$  is non-diagonal and depends explicitly upon the vector separation  $\mathbf{R}_{\alpha\beta}$  of the two indicated atoms, but not upon the individual laboratory-frame positions  $\mathbf{R}_\alpha$  and  $\mathbf{R}_\beta$  of the two atoms, nor upon the position vectors of the other atoms in the aggregate. The particularly simple form of Eq. (20) is largely a consequence of the orthogonality of the spectral-product basis, the use of atomic eigenstates in the representation, and the atomic pairwise-additive nature of the interaction terms in the Hamiltonian operator of Eqs. (2) to (4).

The specific forms of the atomic-energy and pairwise-atomic interaction-energy matrices of Eq. (20) depend upon the choice of ordering rule adopted in Eq. (15). Employing, for example, the common “odometer” ordering convention of letting later indices run to completion prior to earlier ones, the last atomic matrix  $\mathbf{H}^{(N)}$  and the pairwise interaction-energy matrix  $\mathbf{V}^{(N-1,N)}(\mathbf{R}_{N-1,N})$  for the last two atoms are seen to take block diagonal forms, with matrices constructed in the appropriate atomic and atomic-pair product states, respectively, appearing repeatedly down their diagonals. The atomic-energy and pairwise-atomic interaction-energy matrices of Eq. (20) for an arbitrary pair of atoms  $(\alpha, \beta)$  can be obtained in this convention by starting from the block diagonal versions of these matrices and performing appropriate row and column interchanges which are determined by the positions of  $\alpha$  and  $\beta$  relative to the last two indices  $N-1$  and  $N$ , respectively, enumerating the atoms.

Regardless of the choice of ordering convention implied by the label  $O$  of Eq. (15), the atomic matrices can always be written as the ordered outer products

$$\mathbf{H}^{(\alpha)} = \left\{ \mathbf{I}_p^{(1)} \otimes \mathbf{I}_p^{(2)} \otimes \cdots \mathbf{E}_p^{(\alpha)} \otimes \cdots \mathbf{I}_p^{(N)} \right\}_O, \quad (21)$$

where

$$\mathbf{E}_p^{(\alpha)} = \langle \Phi_p^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha) | \hat{H}^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha) | \Phi_p^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha) \rangle \quad (22)$$

is the diagonal matrix of physical eigenenergies of the atom  $\alpha$  [Eqs. (9) to (11)], arranged by convention in energy-increasing order down the diagonal. The interaction-energy matrices are correspondingly written

$$\mathbf{V}^{(\alpha,\beta)}(\mathbf{R}_{\alpha\beta}) = \left\{ \mathbf{I}_p^{(1)} \otimes \mathbf{I}_p^{(2)} \otimes \cdots \mathbf{v}^{(\alpha,\beta)}(\mathbf{R}_{\alpha\beta}) \otimes \cdots \mathbf{I}_p^{(N)} \right\}_O, \quad (23)$$

where

$$\mathbf{v}^{(\alpha,\beta)}(\mathbf{R}_{\alpha\beta}) = \langle \Phi^{(\alpha,\beta)}(\mathbf{i}; \mathbf{j} : \mathbf{R}_{\alpha\beta}) | \hat{V}^{(\alpha,\beta)}(\mathbf{i}; \mathbf{j} : \mathbf{R}_{\alpha\beta}) | \Phi^{(\alpha,\beta)}(\mathbf{i}; \mathbf{j} : \mathbf{R}_{\alpha\beta}) \rangle \quad (24)$$

is the interaction-energy matrix in the ordered atomic-product basis for the  $(\alpha, \beta)$  pair, given by the expression

$$\Phi^{(\alpha,\beta)}(\mathbf{i}; \mathbf{j} : \mathbf{R}_{\alpha\beta}) = \left\{ \Phi_p^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha) \otimes \Phi_p^{(\beta)}(\mathbf{j} : \mathbf{R}_\beta) \right\}_O. \quad (25)$$

In Eqs. (21) to (25),  $\mathbf{I}_p^{(\alpha)}$  is the unit matrix expressing the orthonormality of the antisymmetric atomic spectral basis [Eq. (9)], an outer-matrix-product convention is adopted for the multiplication of matrices enclosed in the brackets  $\{\dots\}$ , and the subscript “ $O$ ” implies ordering of the terms in the energy matrices  $\mathbf{H}^{(\alpha)}$ ,  $\mathbf{V}^{(\alpha,\beta)}(\mathbf{R}_{\alpha\beta})$  and vectors  $\Phi^{(\alpha,\beta)}(\mathbf{i}; \mathbf{j} : \mathbf{R}_{\alpha\beta})$  in accordance with the positions of the individual functions in the row vector of Eq. (15). The pair-product states of Eq. (25) are written for notational simplicity as functions of the vector separation  $\mathbf{R}_{\alpha\beta}$ , rather than of the two position vectors  $\mathbf{R}_\alpha$  and  $\mathbf{R}_\beta$ , in accordance with primary interest here in their use in evaluation of  $\mathbf{v}^{(\alpha,\beta)}(\mathbf{R}_{\alpha\beta})$ .

As should be clear from the discussion of Section 3, the functions  $\Phi^{(\alpha,\beta)}(\mathbf{i}; \mathbf{j} : \mathbf{R}_{\alpha\beta})$  span the totally antisymmetric representation of  $S_{n_\alpha+n_\beta}$  once and only once, but also span other irreducible representations of the  $\alpha, \beta$  atomic-pair permutation group, and so these functions do not warrant a subscript “ $p$ ” designating a physical subspace of the generally reducible product of Eq. (25). It should also be clear that the matrix  $\mathbf{E}_p^{(\alpha)}$  of Eq. (22) in the atomic spectral basis  $\alpha$  has a dimension smaller than that of the matrix  $\mathbf{v}^{(\alpha,\beta)}(\mathbf{R}_{\alpha\beta})$  of Eq. (24) in the  $\alpha, \beta$  atomic-product spectral basis, although the matrices  $\mathbf{H}^{(\alpha)}$  and  $\mathbf{V}^{(\alpha,\beta)}(\mathbf{R}_{\alpha\beta})$  of Eqs. (21) and (23), respectively, have the same dimension as the entire spectral-product basis of Eq. (15).

The vector dependence of  $\mathbf{v}^{(\alpha,\beta)}(\mathbf{R}_{\alpha\beta})$  upon  $\mathbf{R}_{\alpha\beta}$  indicated in Eq. (24) arises from the dependence of the product basis of Eq. (25) on both the magnitude and the angular orientation of the vector  $\mathbf{R}_{\alpha\beta}$  in the laboratory frame. Using the transformation properties of the atomic basis functions under rotations,<sup>65</sup> the interaction-energy matrix of Eq. (24) is given by the expression<sup>54</sup>

$$\mathbf{v}^{(\alpha,\beta)}(\mathbf{R}_{\alpha\beta}) = \mathbf{R}^{(\alpha,\beta)}(\hat{\mathbf{R}}_{\alpha\beta})^\dagger \cdot \mathbf{v}^{(\alpha,\beta)}(R_{\alpha\beta}) \cdot \mathbf{R}^{(\alpha,\beta)}(\hat{\mathbf{R}}_{\alpha\beta}), \quad (26)$$

where  $\mathbf{R}^{(\alpha,\beta)}(\hat{\mathbf{R}}_{\alpha\beta}) = \{\mathbf{D}^{(\alpha)}(\hat{\mathbf{R}}_{\alpha\beta}) \otimes \mathbf{D}^{(\beta)}(\hat{\mathbf{R}}_{\alpha\beta})\}_O$  is an ordered outer product of Wigner rotation matrices for each atom effecting the transformation from a reference orientation in which the two  $z$  axes of the interacting atoms are co-aligned to one in which they take their physical orientations in the laboratory frame.<sup>65</sup> The irreducible interaction-energy matrix  $\mathbf{v}^{(\alpha,\beta)}(R_{\alpha\beta})$  of Eq. (26), which is obtained from Eq. (24) evaluated in the co-aligned reference frame, depends only upon the scalar separation of the two atoms  $R_{\alpha\beta}$ , whereas the notation  $\hat{\mathbf{R}}_{\alpha\beta} (\equiv \phi_{\alpha\beta}, \theta_{\alpha\beta}, 0)$  employed in the Wigner functions in Eq. (26) refers to the two angles specifying the direction of the vector  $\mathbf{R}_{\alpha\beta}$  in the laboratory frame.

Once the matrices of Eqs. (22) and (24) have been constructed, those of Eqs. (21) and (23) must be assembled by performing the row and column re-orderings implied by the symbol “ $O$ ”. Although the dimension of the resulting Hamiltonian matrix of Eq. (20) grows exponentially with the number of atoms considered [ $\approx O(B^N)$  for large numbers  $N$  of identical atoms with  $B$  basis states each], the pairwise nature of the interaction terms of Eq. (4) insures that nonzero matrix elements are obtained only between aggregate spectral-product states that differ by no more than two atomic eigenstates, not unlike the familiar Slater’s rules for two-electron atomic matrix elements between determinantal wave functions comprised of orthonormal orbitals.<sup>63,66</sup> Accordingly,  $\mathbf{H}(\mathbf{R})$  is a sparse matrix which contains non-zero elements the number of which in any row or column grows only as the square of the number of atoms  $N$  and of the number of basis functions  $B$  [ $\approx$

$O(N^2 B^2)$ ], rather than exponentially, with large numbers of atoms and basis functions. The latter observation follows from the number of spectral-product functions that can differ from a given spectral product by zero, one, or two individual atomic labels, and insures that  $\mathbf{H}(\mathbf{R})$  grows more sparse as  $N$  and  $B$  increase. These circumstances, and the fact that the locations of the non-zero elements in any row or column of the matrix of Eq. (23) are known *a priori*, suggest that techniques familiar from large-scale configuration-interaction methods,<sup>63</sup> including particularly recursive or unitary group methods which avoid construction of the entire Hamiltonian matrix at any one time, can be employed in obtaining the eigensolutions of Eq. (17), issues addressed separately below.

## 4.2 Evaluation of Atomic-Energy and Interaction-Energy Matrices

The atomic-energy matrices of Eq. (22) can be evaluated once and for all employing conventional electronic structure theory in its various forms<sup>59–63</sup> in constructing the large denumerable spectrum of eigenfunctions generally required to satisfy the completeness conditions of Eq. (16). Of course, highly accurate experimental values are also generally available for a significant number of the low-lying atomic energies of most atoms.<sup>67</sup> Accordingly, adopting a commonly employed stratagem, the available experimental values, possibly corrected to Coulombic limits by approximate removal of relativistic contributions,<sup>68,69</sup> can be employed in place of the calculated low-lying values, which are generally less accurate than the former, whereas the calculated higher-lying values can be employed as a pseudospectrum of energies in place of the actual Rydberg and continuum atomic states.<sup>70</sup> Such a calibration procedure,<sup>46</sup> which is easily incorporated into the Hamiltonian of Eqs. (20) to (26), is particularly required in cases where the calculated low-lying atomic energies are not in accord with the energy orderings of the experimental spectra. Employing this atomic calibration, the potential energy surfaces obtained from the development are guaranteed to dissociate into accurate atomic separation limits, with calculations required only to provide (Coulombic) interaction energies among the atomic constituents, rather than the absolute values of the total aggregate energies. Of course, in many cases such an atomic calibration procedure will be unnecessary, and the calculated atomic energies can be employed without modification directly in construction of the Hamiltonian matrix.

The integrals required in the irreducible pairwise interaction-energy matrices of Eq. (26) are seen to be two-center, one- and two-electron Coulombic integrals, which can all be calculated in closed analytical forms when Gaussian<sup>39–44</sup> or Slater-like<sup>71,72</sup> orbitals are employed, ensuring that high precision can be achieved in their evaluation. Specifically, the irreducible interaction-energy matrix appearing in Eq. (26) is written in the form

$$\mathbf{v}^{(\alpha,\beta)}(R_{\alpha\beta}) = \int_{\mathbf{r}_\alpha} d\mathbf{r}_\alpha \int_{\mathbf{r}_\beta} d\mathbf{r}_\beta \{ \gamma^{(\alpha)}(\mathbf{r}_\alpha) \otimes \gamma^{(\beta)}(\mathbf{r}_\beta) \} \hat{V}^{(\alpha,\beta)}(\mathbf{r}_\alpha; \mathbf{r}_\beta : R_{\alpha\beta}) \quad (27)$$

using Eq. (24), where [cf., Eq. (4)]

$$\hat{V}^{(\alpha,\beta)}(\mathbf{r}_\alpha; \mathbf{r}_\beta : R_{\alpha\beta}) = \frac{Z_\alpha Z_\beta e^2}{R_{\alpha\beta}} - \frac{Z_\beta e^2}{|\mathbf{r}_\alpha - \mathbf{R}_\beta|} - \frac{Z_\alpha e^2}{|\mathbf{r}_\beta - \mathbf{R}_\alpha|} + \frac{e^2}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|} \quad (28)$$

is the two-center Coulombic interaction operator in the co-aligned coordinate system,  $\mathbf{R}_\alpha = R_\alpha \hat{\mathbf{k}}$  and  $\mathbf{R}_\beta = R_\beta \hat{\mathbf{k}}$ , with  $\hat{\mathbf{k}}$  the unit vector along the co-aligned  $z$  axes, and

$$\gamma^{(\alpha)}(\mathbf{r}_\alpha) = \langle \Phi_p^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha) | \sum_i^{n_\alpha} \delta(\mathbf{r}_\alpha - \mathbf{r}_i) | \Phi_p^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha) \rangle \quad (29)$$

is the so-called one-electron transition density matrix for atom  $\alpha$ ,<sup>73–75</sup> with a similar expression employed for atom  $\beta$ .

Evidently, the Hermitian matrices of Eq. (29), properties of which have been discussed previously in the context of nuclear spectroscopy and nucleon scattering by nuclei,<sup>73–75</sup> determine the associated irreducible interaction-energy matrices of Eqs. (26) and (27), and so constitute the computational invariants required in the development of Eqs. (20) to (26). The matrices of Eq. (29) formally involve all the eigenstates of an individual atom, and so they differ from so-called “reduced” one-electron density matrices, which are scalar functions appropriate for individual atomic eigenstates.<sup>62</sup> Rather, the diagonal elements of the matrix  $\gamma^{(\alpha)}(\mathbf{r}_\alpha)$  are the one-electron charge-density distributions of the spectral eigenstates of atom  $\alpha$ , whereas the off-diagonal elements give the one-electron transition densities connecting these eigenstates. These quantities can be stored in the form of matrices  $\mathbf{\Gamma}^{(\alpha)}$  in the combined atomic-state orbital-basis  $(\Gamma_\alpha, \gamma_\alpha)$  representation, and employed in Eq. (27) in repeated “on-the-fly” calculations of the interaction energies required in construction of the Hamiltonian matrix for the atomic configurations  $\mathbf{R}$  considered. Alternatively, the pairwise interaction-energy matrices of Eq. (27) can be tabulated on a grid of interatomic separations  $R_{\alpha\beta}$  for the interacting atomic pairs of interest and retained for repeated Hamiltonian assembly. Accordingly, in this approach, large-scale configuration-interaction calculations of the atomic spectral states need be performed only once, and the associated one-electron transition-density or interaction-energy matrices retained for repeated use, avoiding explicit high-level molecular configuration-interaction or related calculations involving antisymmetric aggregate many-electron basis states at different aggregate configurations.

### 4.3 Eigenspectrum of the Spectral-Product Hamiltonian Matrix

Although the development of Eqs. (1) to (29) can be employed directly in computational applications in selected cases, a number of factors mitigate against adopting such an approach more generally. Specifically, the spectrum [Eq. (1)] of the Hamiltonian operator of Eqs. (2) to (4) contains the aforementioned unphysical states, including continua in which the physical solutions are embedded when any one atom in the aggregate contains three or more electrons.<sup>32–37</sup> Accordingly, approximations to the physical states of Eqs. (1) to (4) in the full spectral-product basis may generally not be easily discernible among the unphysical quasi-continuum states also spanned by the basis, and may, in fact, be computationally inaccessible in the presence of the afore-mentioned low-energy non-Pauli states present which are associated with over-filled inner-shell configurations and their corresponding continua. This situation is complicated by the fact that precise antisymmetry will only be obtained from the development of Eqs. (1) to (29) in the limit of spectral closure, making identification of the desired physical states potentially subjective.



The task of classifying the states obtained from the Hamiltonian matrix of Eqs. (20) to (29) is further complicated by their degeneracies. Specifically, the pairwise interaction-energy matrices of Eq. (27) will be diagonal in the atomic spin quantum numbers  $S_\alpha, M_{S_\alpha}$  and  $S_\beta, M_{S_\beta}$ , since the Coulomb interaction operator of Eq. (28) is independent of spin coordinates. Consequently, the aggregate Hamiltonian matrix of Eq. (20) will generally factor into noninteracting blocks associated with particular spin configurations of the aggregate atoms ( $S_\alpha, M_{S_\alpha}, \alpha = 1, 2, \dots, N$ ), and the eigensolutions obtained from Eqs. (17) to (29) will generally be fragmented into degenerate orthogonal components associated with these contributing spin configurations. These components must be appropriately combined *ex post facto* to form states of the correct irreducible symmetries.

In a case in which only two different aggregate spin configurations are present in the spectral product basis  $[\Phi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) = \Phi_1(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) \oplus \Phi_2(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R})]$ , for example, Eq. (17) factors into the two independent equations

$$\mathbf{H}_{11}(\mathbf{R}) \cdot \mathbf{U}_1(\mathbf{R}) = \mathbf{U}_1(\mathbf{R}) \cdot \mathbf{E}_1(\mathbf{R}) \quad (30a)$$

$$\mathbf{H}_{22}(\mathbf{R}) \cdot \mathbf{U}_2(\mathbf{R}) = \mathbf{U}_2(\mathbf{R}) \cdot \mathbf{E}_2(\mathbf{R}), \quad (30b)$$

where the off-diagonal matrix elements  $\mathbf{H}_{12}(\mathbf{R})$  and  $\mathbf{H}_{21}(\mathbf{R})$  vanish, and the diagonal energy matrices  $\mathbf{E}_1(\mathbf{R})$ ,  $\mathbf{E}_2(\mathbf{R})$  and solution matrices  $\mathbf{U}_1(\mathbf{R})$ ,  $\mathbf{U}_2(\mathbf{R})$  are obtained from the indicated separate diagonalizations of  $\mathbf{H}_{11}(\mathbf{R})$  and  $\mathbf{H}_{22}(\mathbf{R})$ , respectively. The eigenfunctions of Eq. (19) in this case,

$$\Psi_1(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) = \Phi_1(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) \cdot \mathbf{U}_1(\mathbf{R}) \quad (31a)$$

$$\Psi_2(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) = \Phi_2(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) \cdot \mathbf{U}_2(\mathbf{R}), \quad (31b)$$

may include a solution  $[\Psi_1(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R})]_k$  which in the limit of closure has the same eigenvalue as a solution  $[\Psi_2(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R})]_l$  if both spin configurations can contribute to the total wave function of the chemical aggregate  $[\{\mathbf{E}_1(\mathbf{R})\}_{kk} \approx \{\mathbf{E}_2(\mathbf{R})\}_{ll}]$ . In general, these two components must be identified and appropriately combined to construct the correct antisymmetric aggregate eigenfunction which together they comprise. The two degenerate spin multiplets obtained from Eqs. (31), however, need not necessarily transform irreducibly under electron coordinate-label permutations, and so there may be no way in which to readily identify them *a priori* as potentially degenerate components of a totally antisymmetric physical eigensolution of the Schrödinger equation, particularly in the presence of other nearly degenerate unphysical states. Although these circumstances may seem unfamiliar, a similar situation would arise in treatments of atomic structure employing unrestricted spin-orbital product configurations in constructing the Hamiltonian matrix, rather than Slater determinants.<sup>66</sup> Combinations of products of spatial functions and spin eigenstates,<sup>76,77</sup> or functions of spatial coordinates only,<sup>78</sup> also employed in constructing eigensolutions of irreducible symmetry similarly correspond to solutions expressed in the fragmented forms of Eqs. (30) and (31).

Finally, the factoring of the spectral-product Hamiltonian matrix into individual atomic spin blocks can also lead to a failure to provide the correct numbers of multiplet states in limits of large interatomic separations. This will be so in the common case of dissociations

into open-shell atoms, where the failure to achieve closure in the spectral-product basis in the absence of explicit electron exchange terms can give results which include only the lowest-lying spin multiplet of an allowable number of degenerate states at large atomic separations. These circumstances can lead to calculations of highly unphysical potential energy surfaces which correlate with incorrect dissociation limits. Similar remarks apply to cases in which charge-transfer terms contribute significantly to eigensolutions at large interatomic separations, where the failure to achieve closure in the spectral-product basis and in the corresponding development of Eqs. (17) to (29) could introduce spurious variations in potential energy surfaces with increasing interatomic separations.

## 5.0 Convergence in the Spectral-Product Basis

Group-theoretical methods have been used previously in understanding the consequences of the change in electron-coordinate permutation symmetry group upon formation of atomic aggregates,<sup>32</sup> and have been employed above to verify the presence of the totally antisymmetric representation in the spectral-product basis. Such methods, however, are largely inapplicable to reduction of the basis in the group  $S_{n_t}$  for computational purposes in light of the non-symmetrical nature of the representation and the associated absence of all electron coordinate permutations in explicit form in Eq. (15). In the present Section, the totally antisymmetric representation of  $S_{n_t}$  spanned by the basis of Eq. (15) is isolated, the additional troublesome issues identified in the immediately preceding Section are overcome, and convergence to the correct Schrödinger eigenstates in the antisymmetric subspace of the spectral-product representation is demonstrated.

Symmetry-adapted eigensolutions are devised in the following in the blocked forms

$$\Psi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{N} : \mathbf{R}) = \{\Psi^{(p)}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{N} : \mathbf{R}), \Psi^{(u)}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{N} : \mathbf{R})\}, \quad (32a)$$

$$\mathbf{E}(\mathbf{R}) = \begin{pmatrix} \mathbf{E}_S^{(p)}(\mathbf{R}) & \mathbf{0} \\ \mathbf{0} & \mathbf{E}_S^{(u)}(\mathbf{R}) \end{pmatrix}, \quad (32b)$$

where  $\Psi^{(p)}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R})$  and  $\Psi^{(u)}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R})$  refer to physical “ $p$ ” and unphysical “ $u$ ” solutions of Eqs. (17) to (19), respectively, and  $\mathbf{E}_S^{(p)}(\mathbf{R})$ ,  $\mathbf{E}_S^{(u)}(\mathbf{R})$  are the corresponding diagonal eigenvalue matrices. These eigenspectra are obtained formally from a unitary transformation of the aggregate Hamiltonian matrix of Eq. (20),

$$\mathbf{H}_S(\mathbf{R}) = \mathbf{U}_S(\mathbf{R})^\dagger \cdot \mathbf{H}(\mathbf{R}) \cdot \mathbf{U}_S(\mathbf{R}) \rightarrow \begin{pmatrix} \mathbf{H}_S^{(p)}(\mathbf{R}) & \mathbf{0} \\ \mathbf{0} & \mathbf{H}_S^{(u)}(\mathbf{R}) \end{pmatrix}, \quad (33)$$

which explicitly isolates the physical  $\mathbf{H}_S^{(p)}(\mathbf{R})$  and unphysical  $\mathbf{H}_S^{(u)}(\mathbf{R})$  blocks of the spectral-product Hamiltonian matrix. The unitary transformation matrix  $\mathbf{U}_S(\mathbf{R})$  obtained from diagonalization of the aggregate metric matrix  $\mathbf{S}(\mathbf{R})$  constructed from antisymmetrized spectral-product states is shown to accomplish the blocking of Eqs. (33), and the corresponding eigenfunctions and eigenvalues of Eqs. (32) are shown to converge in the limit of closure to results obtained from standard variational developments employing conventional prior antisymmetry constraints.

## 5.1 Prior Antisymmetry

The development leading to Eqs. (32) and (33) begins with construction of an antisymmetric spectral-product basis, familiar from the early development of Moffitt,<sup>46</sup> obtained employing the prior projection

$$\Phi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) \equiv \hat{P}_A(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n}) \Phi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}), \quad (34)$$

where  $\Phi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R})$  can be taken to be a subspace of Eq. (15) having good total  $M_S$  compatible with the total  $S$  value of interest ( $M_S \leq S$ ). The projector

$$\hat{P}_A(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n}) = (n_1! n_2! \cdots n_N!)^{-1/2} (n_t!)^{-1/2} \sum_{p=1}^{n_t!} (-1)^{\delta_p} \hat{P}_p \quad (35)$$

is the familiar  $n_t$ -electron antisymmetrizer “wave-function normalized” in the limit  $\mathbf{R} \rightarrow \infty$ .<sup>63</sup> In Eq. (35),  $\delta_p$  is the parity of the permutation  $\hat{P}_p$ , the sum is over all  $n_t!$  electron coordinate permutations, and the correction factor  $(n_1! n_2! \cdots n_N!)^{-1/2}$  insures asymptotic wave-function normalization in the presence of the prior antisymmetry of the individual atomic states in Eq. (15). The use of commas between electron coordinates on the left-hand side of Eq. (34) serves to indicate that the individual terms in the basis are of good permutation symmetry type, as opposed to those of the spectral product basis of Eq. (15).

Employing Eqs. (15) and (16), the basis of Eq. (34) is seen to satisfy the closure relation

$$\Phi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) \cdot \Phi(\mathbf{1}', \mathbf{2}', \dots, \mathbf{n}' : \mathbf{R})^\dagger \rightarrow \frac{n_t!}{n_1! n_2! \cdots n_N!} \prod_{\alpha=1}^N \delta_p^{(\alpha)}(\mathbf{i} - \mathbf{i}') \quad (36)$$

in the totally antisymmetric subspace of Eq. (15). Consequently, the antisymmetrized spectral-product or Moffitt basis is formally  $Q$ -fold redundant [ $Q \equiv n_t! / (n_1! n_2! \cdots n_N!)$ ] for representations of antisymmetric states.<sup>25,27–29</sup> To clarify the origins of this circumstance, note that although  $\hat{P}_A$  of Eq. (35) nulls the unphysical irreducible representations of  $S_{n_t}$  contained in the reducible spectral-product basis, the failure to exclude the redundant contributions that arise in antisymmetric states formed from *unrestricted* orbital products in the spectral-product basis gives rise to the factor  $Q$  in Eq. (36). Such overcounting is avoided *within* each individual set of atomic states  $\Phi^{(\alpha)}(\mathbf{i} : \mathbf{R}_\alpha)$  by including all orderings of spin-orbital configurations but excluding explicit permutations among electron coordinates  $\mathbf{i}$ , or, equivalently, by limiting the contributing spin-orbital products to strictly *ordered* electron configurations in Slater determinants.<sup>62</sup> However, since no restrictions are placed on the contributions in Eq. (34) arising from products of spin-orbitals from two or more *different* atomic basis sets, and all electron coordinate permutations among these are included implicitly in the limit of closure, Eq. (34) contains redundant terms in this limit.<sup>25,27–29,73–75</sup> More specifically, the factor  $n_t!$  in the numerator of the redundancy factor  $Q$  is the total number of possible arrangements of  $n_t$  electrons among  $n_t$  available positions, whereas the factor  $n_1! n_2! \cdots n_N!$  in the denominator of  $Q$  corrects this value only for re-arrangements *within* the individual atoms, which do not arise in forming the linearly independent atomic spectral states by using a single assignment of electrons to orbitals or the equivalent restriction to ordered configurations in Slater determinants.<sup>62</sup>

The overcompleteness of Eq. (36) is of no consequence in the limit  $\mathbf{R} \rightarrow \infty$ , since the interaction terms in the Hamiltonian matrix vanish identically and the Hamiltonian matrix correspondingly has no off-diagonal elements. In this case, the states of Eqs. (15) and (34) give the same aggregate energies, and the latter otherwise provides results equivalent to use of the former atomic-product states. Moreover, for large values of  $\mathbf{R}$ , when perturbation theory can be employed, the factor  $Q$  can be taken into account explicitly in expressions for wave functions and energies involving spectral summations, although care must be exercised in this connection.<sup>25–38</sup> More generally, however, for arbitrary finite values of  $\mathbf{R}$ , where the basis of Eq. (34) is no longer orthonormal and perturbation theory is unsuitable, the redundancy in the limit of closure gives rise to linear dependence which must be overcome in computational applications. As will be demonstrated, it is possible to not only employ familiar canonical orthogonalization procedures to remove the linear dependence in Eq. (34),<sup>79</sup> but, correspondingly, to also remove the unwanted non-Pauli representations of the symmetric group  $S_{n_t}$  present in the spectral-product basis of Eq. (15).

## 5.2 Metrically-Defined Hamiltonian Representation

Following standard procedures,<sup>79</sup> the potentially overcomplete Moffitt basis of Eq. (34) is employed in a linear variational solution of the aggregate Schrödinger equation, giving the familiar matrix equation

$$\mathbf{H}(\mathbf{R}) \cdot \mathbf{U}_H(\mathbf{R}) = \mathbf{S}(\mathbf{R}) \cdot \mathbf{U}_H(\mathbf{R}) \cdot \mathbf{E}(\mathbf{R}) \quad (37)$$

appropriate in a non-orthonormal representation.<sup>63</sup> Here,

$$\mathbf{H}(\mathbf{R}) = \sum_{\alpha=1}^N \left\{ \mathbf{H}^{(\alpha)}(\mathbf{R}) + \sum_{\beta=\alpha+1}^N \mathbf{V}^{(\alpha,\beta)}(\mathbf{R}) \right\} \quad (38)$$

is the metrically-defined Hamiltonian matrix in the totally antisymmetric basis, where the individual atomic  $\mathbf{H}^{(\alpha)}(\mathbf{R})$  and atomic-interaction  $\mathbf{V}^{(\alpha,\beta)}(\mathbf{R})$  terms, corresponding to the operators of Eqs. (3) and (4), respectively, are now dependent upon the positions of all the atoms in the aggregate consequent of this antisymmetry [cf., Eq. (20)],

$$\mathbf{S}(\mathbf{R}) = \langle \Phi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) | \Phi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) \rangle \quad (39)$$

is the overlap or metric matrix of the antisymmetric basis,  $\mathbf{E}(\mathbf{R})$  is the aggregate diagonal energy eigenvalue matrix, and  $\mathbf{U}_H(\mathbf{R})$  is the solution matrix that contains the column eigenvector representations of the antisymmetric Schrödinger states in the non-orthogonal basis of Eq. (34),

$$\Psi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) = \Phi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) \cdot \mathbf{U}_H(\mathbf{R}). \quad (40)$$

The matrices  $\mathbf{S}(\mathbf{R})$  and  $\mathbf{U}_H(\mathbf{R})$  together determine the projection of the basis states of Eq. (34) on the solutions of Eq. (40) in the usual form,

$$\langle \Phi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) | \Psi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) \rangle = \mathbf{S}(\mathbf{R}) \cdot \mathbf{U}_H(\mathbf{R}), \quad (41)$$

where  $\mathbf{U}_H(\mathbf{R})$  satisfies the familiar modified orthogonality condition

$$\mathbf{U}_H(\mathbf{R})^\dagger \cdot \mathbf{S}(\mathbf{R}) \cdot \mathbf{U}_H(\mathbf{R}) = \mathbf{I}, \quad (42)$$

and  $\mathbf{I}$  is the unit matrix of dimension equal to that of the basis of Eq. (34). It should be noted that different fonts are employed in Eqs. (17) to (20) and in Eqs. (37) to (42) to distinguish between matrices and other quantities represented in the spectral-product and Moffitt basis sets, respectively.

### 5.3 Removal of Linear Dependence in the Moffitt Basis

In the closure limit of Eq. (36), the Moffitt basis of Eq. (34) is linearly dependent, the metric matrix of Eq. (39) correspondingly becomes singular [ $\det|\mathbf{S}(\mathbf{R})| \rightarrow 0$ ], and Eq. (37) is generally ill conditioned. The linear dependence of the basis of Eq. (34) in the limit of closure is avoided by isolating a linearly independent subspace employing the unitary transformation matrix that diagonalizes  $\mathbf{S}(\mathbf{R})$ ,

$$\mathbf{U}_S(\mathbf{R})^\dagger \cdot \mathbf{S}(\mathbf{R}) \cdot \mathbf{U}_S(\mathbf{R}) = \mathbf{s}_d(\mathbf{R}), \quad (43)$$

where the diagonal matrix  $\mathbf{s}_d(\mathbf{R})$  contains a positive block  $[\mathbf{s}_d^{(p)}(\mathbf{R})]$  and a block  $[\mathbf{s}_d^{(u)}(\mathbf{R})]$  that tends to zero value in the closure limit. By appropriate orderings of the eigenvalues and vectors of  $\mathbf{S}(\mathbf{R})$ , the non-zero block associated with the column eigenvectors in  $\mathbf{U}_S(\mathbf{R})$  that provide the physically significant linearly-independent subspace of Eq. (34) can be placed in the upper left-hand corner of  $\mathbf{s}_d(\mathbf{R})$ , whereas the block that tends to zero, associated with the linearly-dependent or “unwanted” portion of the basis of Eq. (34), can be placed in the lower right-hand corner, giving

$$\mathbf{s}_d(\mathbf{R}) = \begin{pmatrix} \mathbf{s}_d^{(p)}(\mathbf{R}) & \mathbf{0} \\ \mathbf{0} & \mathbf{s}_d^{(u)}(\mathbf{R}) \end{pmatrix} \rightarrow \begin{pmatrix} Q \mathbf{I}_p & \mathbf{0} \\ \mathbf{0} & \mathbf{0}_u \end{pmatrix}. \quad (44)$$

Here,  $\mathbf{I}_p$  is the unit matrix in the linearly-independent physical subspace,  $\mathbf{0}_u$  is the zero matrix in the unwanted subspace, and  $Q$  is the redundancy factor of Eq. (36). The right-hand side of Eq. (44) follows from the observation that the eigenvalues of the metric matrix  $\mathbf{S}(\mathbf{R})$  are either  $Q$  or 0 in the limit of closure, in accordance with the presence of this factor in Eq. (36) and the linear dependence of the unwanted subspace.

Employing the matrix  $\mathbf{U}_S(\mathbf{R})$  of Eq. (43), the basis of Eq. (34) is transformed into a new basis  $\Phi_S(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R})$  comprising the linearly-independent subspace  $\Phi_S^{(p)}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R})$  in which the physical eigenstates can be constructed, and the unwanted subspace  $\Phi_S^{(u)}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R})$ . The two subspaces are given by the common expression

$$\begin{aligned} \Phi_S(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) &= \Phi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) \cdot \mathbf{U}_S(\mathbf{R}) \cdot \mathbf{s}_d(\mathbf{R})^{-1/2} \\ &\equiv \{\Phi_S^{(p)}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}), \Phi_S^{(u)}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R})\}, \end{aligned} \quad (45)$$

where

$$\Phi_S^{(p)}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) = \{\Phi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) \cdot \mathbf{U}_S(\mathbf{R})\}_p \cdot \mathbf{s}_d^{(p)}(\mathbf{R})^{-1/2} \quad (46)$$

is the orthonormal linearly-independent subspace and  $\{\dots\}_p$  designates the physical part of the enclosed row vector. The linearly-dependent subspace

$$\Phi_S^{(u)}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) = \{\Phi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) \cdot \mathbf{U}_S(\mathbf{R})\}_u \cdot \mathbf{s}_d^{(u)}(\mathbf{R})^{-1/2} \quad (47)$$

is ill-defined in the limit  $\mathbf{s}_d^{(u)}(\mathbf{R}) \rightarrow \mathbf{0}_r$  but is not required here. The closure of the physical basis for antisymmetric states,

$$\begin{aligned} & \Phi_S^{(p)}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{N} : \mathbf{R}) \cdot \Phi_S^{(p)}(\mathbf{1}', \mathbf{2}', \dots, \mathbf{N}' : \mathbf{R})^\dagger = \\ & \{\Phi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{N} : \mathbf{R}) \cdot \mathbf{U}_S(\mathbf{R})\}_p \cdot \mathbf{s}_d^{(p)}(\mathbf{R})^{-1} \cdot \{\Phi(\mathbf{1}', \mathbf{2}', \dots, \mathbf{N}' : \mathbf{R}) \cdot \mathbf{U}_S(\mathbf{R})\}_p^\dagger \rightarrow \\ & Q^{-1} \{\Phi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{N} : \mathbf{R}) \cdot \Phi(\mathbf{1}', \mathbf{2}', \dots, \mathbf{N}' : \mathbf{R})\}_p \rightarrow \left\{ \prod_{\alpha=1}^N \delta_p^{(\alpha)}(\mathbf{i} - \mathbf{i}') \right\}_p, \end{aligned} \quad (48)$$

follows from Eqs. (36) and (44) and the unitarity of  $\mathbf{U}_S(\mathbf{R})$ , with the redundancy factors  $Q$  that appear in the numerator and denominator of the left-hand side of the last line in Eq. (48) canceling in the limit of completeness. The second subscript “ $p$ ” on the right-hand side of Eq. (48) refers to restriction of the delta-function product to the linearly-independent subspace.

The matrix  $\mathbf{U}_S(\mathbf{R})$  of Eq. (43) can be employed in the usual way to transform the potentially ill-conditioned Hamiltonian matrix  $\mathbf{H}(\mathbf{R})$  of Eqs. (37) and (38) to a form that isolates its linearly-independent block, giving the generally well-conditioned matrix Schrödinger equation

$$\mathbf{H}_S^{(p)}(\mathbf{R}) \cdot \mathbf{U}_H^{(p)}(\mathbf{R}) = \mathbf{U}_H^{(p)}(\mathbf{R}) \cdot \mathbf{E}_S^{(p)}(\mathbf{R}), \quad (49)$$

where the reduced-dimension matrix

$$\begin{aligned} \mathbf{H}_S^{(p)}(\mathbf{R}) &= \langle \Phi_S^{(p)}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{N} : \mathbf{R}) | \hat{H}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{N} : \mathbf{R}) | \Phi_S^{(p)}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{N} : \mathbf{R}) \rangle \\ &= \mathbf{s}_d^{(p)}(\mathbf{R})^{-1/2} \cdot \{\mathbf{U}_S(\mathbf{R})^\dagger \cdot \mathbf{H}(\mathbf{R}) \cdot \mathbf{U}_S(\mathbf{R})\}_{pp} \cdot \mathbf{s}_d^{(p)}(\mathbf{R})^{-1/2} \\ &\rightarrow Q^{-1/2} \{\mathbf{U}_S(\mathbf{R})^\dagger \cdot \mathbf{H}(\mathbf{R}) \cdot \mathbf{U}_S(\mathbf{R})\}_{pp} Q^{-1/2} \\ &\equiv \sum_{\alpha=1}^N \left\{ \mathbf{H}_S^{(\alpha)}(\mathbf{R}) + \sum_{\beta=\alpha+1}^N \mathbf{V}_S^{(\alpha, \beta)}(\mathbf{R}) \right\} \end{aligned} \quad (50)$$

provides the non-singular portion of the metrically-defined Hamiltonian matrix. Here, the notation  $\{\dots\}_{pp}$  implies that only the upper-left ( $pp$ ) block of the enclosed matrix is to be retained, and the individual atomic

$$\begin{aligned} \mathbf{H}_S^{(\alpha)}(\mathbf{R}) &= \mathbf{s}_d^{(p)}(\mathbf{R})^{-1/2} \cdot \{\mathbf{U}_S(\mathbf{R})^\dagger \cdot \mathbf{H}^{(\alpha)}(\mathbf{R}) \cdot \mathbf{U}_S(\mathbf{R})\}_{pp} \cdot \mathbf{s}_d^{(p)}(\mathbf{R})^{-1/2} \\ &\rightarrow Q^{-1/2} \{\mathbf{U}_S(\mathbf{R})^\dagger \cdot \mathbf{H}^{(\alpha)}(\mathbf{R}) \cdot \mathbf{U}_S(\mathbf{R})\}_{pp} Q^{-1/2} \end{aligned} \quad (51)$$

and atomic-interaction

$$\begin{aligned} \mathbf{V}_{\mathbf{S}}^{(\alpha,\beta)}(\mathbf{R}) &= \mathbf{s}_d^{(p)}(\mathbf{R})^{-1/2} \cdot \{\mathbf{U}_{\mathbf{S}}(\mathbf{R})^\dagger \cdot \mathbf{V}^{(\alpha,\beta)}(\mathbf{R}) \cdot \mathbf{U}_{\mathbf{S}}(\mathbf{R})\}_{pp} \cdot \mathbf{s}_d^{(p)}(\mathbf{R})^{-1/2} \\ &\rightarrow Q^{-1/2} \{\mathbf{U}_{\mathbf{S}}(\mathbf{R})^\dagger \cdot \mathbf{V}^{(\alpha,\beta)}(\mathbf{R}) \cdot \mathbf{U}_{\mathbf{S}}(\mathbf{R})\}_{pp} Q^{-1/2} \end{aligned} \quad (52)$$

terms in Eq. (50) refer to transformations of the corresponding terms in Eq. (38).

The matrix of physical energies  $\mathbf{E}_{\mathbf{S}}^{(p)}(\mathbf{R})$  and of corresponding column eigenvectors  $\mathbf{U}_{\mathbf{H}}^{(p)}(\mathbf{R})$  of Eq. (49) are of reduced dimensions relative to  $\mathbf{E}(\mathbf{R})$  and  $\mathbf{U}_{\mathbf{H}}(\mathbf{R})$  of Eq. (37), respectively. Since the eigenstates  $\Phi_{\mathbf{S}}^{(p)}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R})$  of the  $\mathbf{S}(\mathbf{R})$  matrix of Eq. (41) are symmetry adapted, the Hamiltonian matrix of Eq. (50) will be block diagonal in the total spin quantum numbers and in other appropriate aggregate symmetry labels, in accordance with Schur's lemmas.<sup>60</sup> Of course, the limits  $\mathbf{s}_d^{(p)}(\mathbf{R}) \rightarrow Q \mathbf{I}_p$  and  $\mathbf{s}_d^{(u)}(\mathbf{R}) \rightarrow \mathbf{0}_u$  of Eq. (44) apply only when closure is achieved, with the partitioning of  $\mathbf{s}_d(\mathbf{R})$  into  $\mathbf{s}_d^{(p)}(\mathbf{R})$  and  $\mathbf{s}_d^{(u)}(\mathbf{R})$  somewhat subjective, and the diagonal matrix  $\mathbf{s}_d^{(p)}(\mathbf{R})$  appearing in Eqs. (50) to (52) required more generally, rather than its limiting value  $Q \mathbf{I}_p$ . As a consequence, selection of the dimension of the physical block  $\{\dots\}_{pp}$  of the transformed Hamiltonian matrix, which will generally have non-zero off-diagonal blocks connecting the “ $p$ ” and “ $u$ ” subspaces in finite representations, is correspondingly subjective, and must be determined in the course of calculations on basis of the accuracy of results desired, with convergence achieved when the off-diagonal terms are judged to be negligible.

#### 5.4 Isolation of the Antisymmetric Spectral-Product Subspace

The foregoing standard development employed to remove linear dependence in the prior antisymmetrized or Moffitt basis of Eq. (34) can also be employed to separate the physical and unphysical subspaces of the spectral-product representation, and to construct corresponding energies and eigenfunctions of the Hamiltonian matrix of Eq. (17) which converge to the symmetry-adapted eigenstates obtained from the development of Eqs. (37) to (52). Specifically, the important identity

$$\langle \Phi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) | \hat{P}_A(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n}) | \Phi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) \rangle = Q^{-1/2} \mathbf{S}(\mathbf{R}), \quad (53)$$

which follows from substitution of Eq. (34) into Eq. (39) and is valid in any denumerable basis, indicates that the matrix representative of the antisymmetric projector of Eq. (35) in the spectral-product basis is proportional to the metric matrix  $\mathbf{S}(\mathbf{R})$  constructed in the antisymmetric basis  $\Phi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R})$ . Accordingly, diagonalization of the matrix  $\mathbf{S}(\mathbf{R})$  in Eq. (43) is equivalent to diagonalization of the matrix representative of the antisymmetric projector in the spectral-product basis, and to the construction of a subspace of antisymmetric eigenstates in this representation.

Applying the transformation  $\mathbf{U}_{\mathbf{S}}(\mathbf{R})$  to Eq. (53) gives

$$\begin{aligned} \mathbf{U}_{\mathbf{S}}(\mathbf{R})^\dagger \cdot \langle \Phi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) | \hat{P}_A(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n}) | \Phi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) \rangle \cdot \mathbf{U}_{\mathbf{S}}(\mathbf{R}) \\ = Q^{-1/2} \begin{pmatrix} \mathbf{s}_d^{(p)}(\mathbf{R}) & \mathbf{0} \\ \mathbf{0} & \mathbf{s}_d^{(u)}(\mathbf{R}) \end{pmatrix}, \end{aligned} \quad (54)$$

where Eq. (43) has been employed on the right-hand side. Defining the transformed basis

$$\begin{aligned}\Phi_{\mathbf{S}}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) &= \Phi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) \cdot \mathbf{U}_{\mathbf{S}}(\mathbf{R}) \\ &\equiv \{\Phi_{\mathbf{S}}^{(p)}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}), \Phi_{\mathbf{S}}^{(u)}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R})\},\end{aligned}\quad (55)$$

where

$$\Phi_{\mathbf{S}}^{(p/u)}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) = \{\Phi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) \cdot \mathbf{U}_{\mathbf{S}}(\mathbf{R})\}_{p/u} \quad (56)$$

correspond to the physical and unphysical subspaces, it follows that Eq. (54) can be written as the two equations

$$\langle \Phi_{\mathbf{S}}^{(p)}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) | \frac{1}{n_t!} \sum_{p=1}^{n_t!} (-1)^{\delta_p} \hat{P}_p | \Phi_{\mathbf{S}}^{(p)}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) \rangle = \mathbf{s}_d^{(p)}(\mathbf{R})/Q \rightarrow \mathbf{I}_p \quad (57a)$$

$$\langle \Phi_{\mathbf{S}}^{(u)}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) | \frac{1}{n_t!} \sum_{p=1}^{n_t!} (-1)^{\delta_p} \hat{P}_p | \Phi_{\mathbf{S}}^{(u)}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) \rangle = \mathbf{s}_d^{(u)}(\mathbf{R})/Q \rightarrow \mathbf{0}_u. \quad (57b)$$

Equation (57a) demonstrates, independent of group-theoretical considerations,<sup>60</sup> that the “ $p$ ” subspace of Eqs. (55) and (56) contains the totally antisymmetric representation of  $S_{n_t}$  only once  $[\mathbf{s}_d^{(p)}(\mathbf{R})/Q \rightarrow \mathbf{I}_p]$ , whereas Eq. (57b) demonstrates that the “ $u$ ” subspace consists of non-totally-antisymmetric eigenstates in the limit of closure  $[\mathbf{s}_d^{(u)}(\mathbf{R})/Q \rightarrow \mathbf{0}_r]$ . Note that the factor  $(1/n_t!)$  employed in Eqs. (57) is appropriate for a normalized Young operator, rather than a normalized wave function [cf., Eq. (35)]. Finally, from Eqs. (16) and (56) and the unitarity of  $\mathbf{U}_{\mathbf{S}}(\mathbf{R})$ ,

$$\Phi_{\mathbf{S}}^{(p/u)}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) \cdot \Phi_{\mathbf{S}}^{(p/u)}(\mathbf{1}'; \mathbf{2}'; \dots; \mathbf{n}' : \mathbf{R})^\dagger \rightarrow \left\{ \prod_{\alpha=1}^N \delta_p^{(\alpha)}(\mathbf{i} - \mathbf{i}') \right\}_{p/u} \quad (58)$$

expresses the closure of both subspaces of the eigenstates of the totally antisymmetric projector in the spectral-product basis.

It is seen from the development of Eqs. (53) to (58) that both “ $p$ ” and “ $u$ ” subspaces of Eqs. (55) and (56) can be constructed employing the transformation matrix of Eq. (43) obtained from the metric matrix, with “ $p$ ” referring to the totally antisymmetric physical subspace of the spectral-product basis and “ $u$ ” to a mathematically well-defined orthonormal unphysical subspace in this representation. It may be concluded, therefore, that the transformation matrix  $\mathbf{U}_{\mathbf{S}}(\mathbf{R})$  of Eq. (43), defined to eliminate linear dependence in the explicitly antisymmetrized Moffitt basis  $\Phi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R})$  of Eq. (34), correspondingly separates the totally antisymmetric and non-Pauli subspaces of the spectral-product basis  $\Phi(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R})$  of Eq. (15). Accordingly,  $\mathbf{U}_{\mathbf{S}}(\mathbf{R})$  can be employed to partition the Hamiltonian matrix of Eq. (20) into its physical and unphysical blocks [Eq. (33)], and to construct physical Schrödinger eigenstates in the spectral-product basis [Eqs. (32)].

Employing the transformation matrix  $\mathbf{U}_{\mathbf{S}}(\mathbf{R})$  of Eq. (43), the physical block of the matrix Schrödinger equation in the spectral-product basis [Eq. (17)] takes the form [cf., Eq. (49)]

$$\mathbf{H}_{\mathbf{S}}^{(p)}(\mathbf{R}) \cdot \mathbf{U}_{\mathbf{H}}^{(p)}(\mathbf{R}) = \mathbf{U}_{\mathbf{H}}^{(p)}(\mathbf{R}) \cdot \mathbf{E}_{\mathbf{S}}^{(p)}(\mathbf{R}), \quad (59)$$



where

$$\begin{aligned} \mathbf{H}_{\mathbf{S}}^{(p)}(\mathbf{R}) &= \langle \Phi_{\mathbf{S}}^{(p)}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{N} : \mathbf{R}) | \hat{H}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{N} : \mathbf{R}) | \Phi_{\mathbf{S}}^{(p)}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{N} : \mathbf{R}) \rangle \\ &= \{ \mathbf{U}_{\mathbf{S}}^{\dagger}(\mathbf{R}) \cdot \mathbf{H}(\mathbf{R}) \cdot \mathbf{U}_{\mathbf{S}}(\mathbf{R}) \}_{pp} \equiv \sum_{\alpha=1}^N \left\{ \mathbf{H}_{\mathbf{S}}^{(\alpha)}(\mathbf{R}) + \sum_{\beta=\alpha+1}^N \mathbf{V}_{\mathbf{S}}^{(\alpha,\beta)}(\mathbf{R}) \right\} \end{aligned} \quad (60)$$

is the physical block of the Hamiltonian matrix of Eq. (20), with

$$\mathbf{H}_{\mathbf{S}}^{(\alpha)}(\mathbf{R}) = \{ \mathbf{U}_{\mathbf{S}}(\mathbf{R})^{\dagger} \cdot \mathbf{H}^{(\alpha)} \cdot \mathbf{U}_{\mathbf{S}}(\mathbf{R}) \}_{pp}, \quad (61)$$

and

$$\mathbf{V}_{\mathbf{S}}^{(\alpha,\beta)}(\mathbf{R}) = \{ \mathbf{U}_{\mathbf{S}}(\mathbf{R})^{\dagger} \cdot \mathbf{V}^{(\alpha,\beta)}(\mathbf{R}_{\alpha\beta}) \cdot \mathbf{U}_{\mathbf{S}}(\mathbf{R}) \}_{pp}, \quad (62)$$

corresponding to transformations of the individual terms of Eqs. (21) and (23), now dependent upon the positions of all the atoms in the aggregate as a consequence of the non-local effects of antisymmetry.

### 5.5 Equivalence of Prior and Post Antisymmetrization

To demonstrate the equivalence of results obtained from the post and prior antisymmetrization procedures described in the foregoing developments, note from Eq. (34) that the states  $\Phi_{\mathbf{S}}^{(p)}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R})$  and  $\Phi_{\mathbf{S}}^{(p)}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R})$  of Eqs. (46) and (56) are identical in the limit of closure,

$$\begin{aligned} \Phi_{\mathbf{S}}^{(p)}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) &= \hat{P}_A \Phi_{\mathbf{S}}^{(p)}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) \cdot \mathbf{s}_d^{(p)}(\mathbf{R})^{-1/2} \rightarrow \\ (n_t!)^{-1} \sum_{p=1}^{n_t!} (-1)^{\delta_p} \hat{P}_p \Phi_{\mathbf{S}}^{(p)}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) &\rightarrow \Phi_{\mathbf{S}}^{(p)}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}), \end{aligned} \quad (63)$$

where the left-hand side of the last line is a consequence of Eq. (44) and the right-hand side of the antisymmetry of the basis  $\Phi_{\mathbf{S}}^{(p)}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R})$  in the limit of closure, the  $n_t!$  permutations of the unnormalized antisymmetrizer  $\sum_{p=1}^{n_t!} (-1)^{\delta_p} \hat{P}_p$  providing  $n_t!$  identical terms which cancel the corresponding factor in the denominator in this limit. Alternatively, employing Eqs. (53) to (57), the spectral overlap of the two sets of basis states is given by the expression

$$\langle \Phi_{\mathbf{S}}^{(p)}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) | \Phi_{\mathbf{S}}^{(p)}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) \rangle = Q^{-1/2} \mathbf{s}_d^{(p)}(\mathbf{R})^{1/2} \rightarrow \mathbf{I}_p, \quad (64)$$

in accordance with these basis states becoming term-by-term identical functions in the closure limit of Eq. (63).

The foregoing results can also be expressed in terms of the representation of the transformed Moffitt basis [Eq. (46)] in the transformed spectral-product basis [Eq. (56)],

$$\Phi_{\mathbf{S}}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) = \Phi_{\mathbf{S}}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) \cdot \langle \Phi_{\mathbf{S}}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) | \Phi_{\mathbf{S}}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{N} : \mathbf{R}) \rangle \rightarrow$$

$$\Phi_{\mathbf{S}}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) \cdot Q^{-1/2} \mathbf{s}_d(\mathbf{R}) \cdot \mathbf{s}_d(\mathbf{R})^{-1/2} \rightarrow \Phi_{\mathbf{S}}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) \cdot \begin{pmatrix} \mathbf{I}_p & \mathbf{0} \\ \mathbf{0} & \mathbf{0}_u \end{pmatrix}, \quad (65)$$

employing Eqs. (53) to (57) and the closure limit in the last line. It is seen that Eq. (65) corresponds to Eq. (63) for the physical subspaces of the two basis sets, and also exhibits explicitly the linear dependence of the subspace  $\Phi_{\mathbf{S}}^{(u)}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R})$  in the limit of closure.

Similarly, introducing the closure relation of Eq. (58) for the physical states on either side of the Hamiltonian operator in Eq. (50), and using Eq. (64), gives

$$\begin{aligned} H_{\mathbf{S}}^{(p)}(\mathbf{R}) &= \langle \Phi_{\mathbf{S}}^{(p)}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) | \hat{H}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) | \Phi_{\mathbf{S}}^{(p)}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) \rangle \\ &= Q^{-1/2} \mathbf{s}_d^{(p)}(\mathbf{R})^{1/2} \cdot \mathbf{H}_{\mathbf{S}}^{(p)}(\mathbf{R}) \cdot \mathbf{s}_d^{(p)}(\mathbf{R})^{1/2} Q^{-1/2} \rightarrow \mathbf{H}_{\mathbf{S}}^{(p)}(\mathbf{R}), \end{aligned} \quad (66)$$

employing the limiting expression  $\mathbf{s}_d^{(p)}(\mathbf{R}) \rightarrow Q \mathbf{I}_p$  in the last line, where  $\mathbf{H}_{\mathbf{S}}^{(p)}(\mathbf{R})$  is given by Eq. (60). The individual atomic

$$\mathbf{H}_{\mathbf{S}}^{(\alpha)}(\mathbf{R}) = Q^{-1/2} \mathbf{S}_d^{(p)}(\mathbf{R})^{+1/2} \cdot \mathbf{H}_{\mathbf{S}}^{(\alpha)}(\mathbf{R}) \cdot \mathbf{S}_d^{(p)}(\mathbf{R})^{+1/2} Q^{-1/2} \rightarrow \mathbf{H}_{\mathbf{S}}^{(\alpha)}(\mathbf{R}) \quad (67)$$

and pair-interaction

$$\mathbf{V}_{\mathbf{S}}^{(\alpha, \beta)}(\mathbf{R}) = Q^{-1/2} \mathbf{S}_d^{(p)}(\mathbf{R})^{+1/2} \cdot \mathbf{V}_{\mathbf{S}}^{(\alpha, \beta)}(\mathbf{R}) \cdot \mathbf{S}_d^{(p)}(\mathbf{R})^{+1/2} Q^{-1/2} \rightarrow \mathbf{V}_{\mathbf{S}}^{(\alpha, \beta)}(\mathbf{R}), \quad (68)$$

terms of Eq. (50) are also seen to be equivalent to the corresponding terms  $\mathbf{H}_{\mathbf{S}}^{(\alpha)}(\mathbf{R})$  and  $\mathbf{V}_{\mathbf{S}}^{(\alpha, \beta)}(\mathbf{R})$  appearing in Eqs. (60) to (62) in the limit of closure. Equations (66) to (68) show that the Hamiltonian matrices of Eqs. (50) and (60), and the associated individual atomic-energy and atomic pairwise interaction-energy matrices are related by the indicated renormalizations in finite basis sets, whereas they are identical in the closure limit.

Finally, it follows from the foregoing development that the eigenvalues and eigenvectors obtained from Eq. (59) converge to those of Eq. (49) [ $\mathbf{E}_{\mathbf{S}}^{(p)}(\mathbf{R}) \rightarrow \mathbf{E}_{\mathbf{S}}^{(p)}(\mathbf{R})$ ,  $\mathbf{U}_{\mathbf{H}}^{(p)}(\mathbf{R}) \rightarrow \mathbf{U}_{\mathbf{H}}^{(p)}(\mathbf{R})$ ], and, in view of the equivalence of the two basis sets [Eqs. (63) to (65)], that the eigenstates obtained from the two developments,

$$\Psi^{(p)}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) = \Phi_{\mathbf{S}}^{(p)}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) \cdot \mathbf{U}_{\mathbf{H}}^{(p)}(\mathbf{R}) \quad (69a)$$

$$\Psi^{(p)}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) = \Phi_{\mathbf{S}}^{(p)}(\mathbf{1}; \mathbf{2}; \dots; \mathbf{n} : \mathbf{R}) \cdot \mathbf{U}_{\mathbf{H}}^{(p)}(\mathbf{R}), \quad (69b)$$

provide identical antisymmetric solutions of the Schrödinger equation in the limit of closure.

## 6.0 Computational Implementation and Illustrative Calculations

To demonstrate that the new approach described in the foregoing Sections is computationally viable, illustrative calculations of the lowest-lying singlet and triplet states of the electron pair bond ( $\text{H}_2$ ) are given as an example of the nature of the metric matrix of Eq. (39) and its eigenvalues, and of the convergence achieved employing standard Gaussian basis-set methodology.<sup>39,40</sup> A computationally efficient implementation of the theory is

described which employs recursive construction<sup>80,81</sup> of invariant subspaces of the spectral basis starting from appropriate reference states in calculations of potential-energy curves. Construction of the entire metric matrix is avoided in this way, and only individual rows of the spectral-product Hamiltonian matrix need be evaluated sequentially, avoiding its complete construction and storage at any one time.

### 6.1 Illustrative Calculations - The Electron Pair Bond

In the two-electron case ( $n_t=2$ ), the spin functions are factored out and attention focused on spatial functions which are symmetric or antisymmetric under electron transposition. These provide a basis for irreducible representations of  $S_2$  corresponding to single- and triplet-state symmetries, respectively, with the singlet states playing the role of the unphysical subspace in this example. That is, although the spatially symmetric states are physically significant for  $H_2$ , they nevertheless represent an unwanted symmetry type in the context of the development of Section 5 relative to the spatially antisymmetric states, and so can be used to illustrate the permutation-symmetry isolation method described there. In the absence of other irreducible representations for  $n_t=2$ , both sets of solutions can also be constructed by direct diagonalization of the spectral-product Hamiltonian matrix for comparison with results obtained from the unitary transformation of Eqs. (59) to (62) for isolating the subspace representations.

The spectral-product basis of Eq. (15) in this case,

$$\Phi(\mathbf{1}; \mathbf{2} : R) = \left\{ \phi^{(\alpha)}(\mathbf{1} : \mathbf{R}_\alpha) \otimes \phi^{(\beta)}(\mathbf{2} : \mathbf{R}_\beta) \right\}_O, \quad (70)$$

corresponds formally to all products of all discrete and continuum hydrogenic orbitals for the two atoms, here designated as  $\alpha$  and  $\beta$ , with  $R = |\mathbf{R}_\alpha - \mathbf{R}_\beta|$  the interatomic separation. The basis of Eq. (70) spans both spatially symmetric and antisymmetric representations of the group  $S_2$  once and only once, whereas its antisymmetric form [Eqs (34) and (35)] will be 2-fold redundant, as is seen from Eq. (36). To avoid dealing explicitly with continuum hydrogenic states, denumerable representational basis sets are employed in the calculations in the usual way.<sup>39,40</sup> Specifically, approximations to the orbital spectra  $\phi^{(\alpha)}(\mathbf{1} : \mathbf{R}_\alpha)$  and  $\phi^{(\beta)}(\mathbf{2} : \mathbf{R}_\beta)$  are devised which accurately reproduce the lowest-lying orbitals and which also span the Rydberg and lower-energy portion of the continuous spectrum in the form of pseudostates.<sup>70</sup> By adopting even-tempered Gaussian basis sets for this purpose,<sup>82</sup> standard computational methods can be employed in evaluating the matrix elements required in forming the spectral-product Hamiltonian matrix [Eqs. (20) to (25)] and in performing its unitary transformation [Eqs. (43) and (60)].<sup>39,40</sup>

In Table 1 is shown the spectrum of atomic energies obtained for  $s, p, d$  and  $f$  orbitals constructed in even-tempered Gaussian basis sets,<sup>82</sup> with orbital exponents chosen so that the discrete and lower continuum states are spanned by the numbers of orbitals shown for each angular momentum value.<sup>83–85</sup> Although systematic studies of orbital selection are not reported here, it should be noted that considerable experience has been gained in this connection through previous studies of square-integrable representations of all the discrete and continuum states of atoms and polyatomic molecules constructed on a common basis.<sup>70</sup> The spectra of Table 1 are judged on basis of their spatial and spectral extent to be suitable for describing the charge distortions accompanying chemical bond or antibond formation in

$\text{H}_2$  in the interval  $R \approx 1$  to  $5 a_0$ , for describing wave function symmetry or antisymmetry in the absence of explicit electron exchange terms, and for otherwise approximating spectral closure in this interval.

In Figure 1 are shown selected eigenvalues of the  $(1,296 \times 1,296)$  metric matrix  $\mathbf{S}(R)$  of Eq. (39) for  $\text{H}_2$  evaluated employing only the  $s$  and  $p$  basis sets of Table 1.<sup>84,85</sup> The normalized two-electron antisymmetrizer,

$$\hat{P}_A(\mathbf{1}, \mathbf{2}) = (1/2)^{-1/2}(1 - \hat{P}_{12}), \quad (71)$$

is employed in this case, with the redundancy factor  $Q=(2!/1!1!)=2$  indicating that the totally antisymmetric representation of  $S_2$  is spanned twice by the antisymmetric spectral-product basis in the limit of closure. Only the fifty largest ( $s_i \approx 2$ ) and the fifty smallest ( $s_i \approx 0$ ) eigenvalues of  $\mathbf{S}(R)$  are shown in Figure 1 as functions of the interatomic separation in  $\text{H}_2$ . The eigenstates of  $\mathbf{S}(R)$  corresponding to  $s_i \approx 2$  values refer to linearly-independent spatially antisymmetric states constructed in the antisymmetric basis, whereas those corresponding to  $s_i \approx 0$  values refer to linearly-dependent combinations of the antisymmetric basis, in accordance with Eqs. (43) to (48). On the other hand, the states obtained in the spectral-product basis corresponding to the  $s_i \approx 2$  of values of  $\mathbf{S}(R)$  refer to antisymmetric states, while those corresponding to  $s_i \approx 0$  values refer to symmetric states, in accordance with Eqs. (53) to (58). When the two-electron symmetric projector is employed in place of Eq. (71), results identical to the foregoing are obtained, but with the states previously corresponding to  $s_i \approx 2$  and  $s_i \approx 0$  interchanging their identities

A significant number of the eigenvalues of  $\mathbf{S}(R)$  depicted in Figure 1 evidently maintain their extreme values ( $s_i \approx 0$  or  $2$ ) over the chemical interaction region ( $R \approx 1$  to  $5 a_0$ ), whereas only a very few of these extend into the van der Waals region ( $R \approx 5$  to  $10 a_0$ ). These behaviors are entirely in accord with the spatial characteristics of the spectral states of Table 1 employed in constructing  $\mathbf{S}(R)$ , which states have relatively small amplitudes at distances  $\approx 5$  to  $10 a_0$  from the atomic origins. Accordingly, the basis of Table 1 can be expected to give converged results in the chemical interaction region, and particularly at the equilibrium interatomic separation ( $R = 1.40 a_0$ ), whereas, alternative or larger basis sets are required to achieve closure at larger interatomic separations.

The spectra of Table 1 are employed in calculations of energies and expectation values for the lowest-lying  $^1\Sigma_g^+$  and  $^3\Sigma_u^+$  states in  $\text{H}_2$  at the equilibrium interatomic separation following the developments of Sections 4 and 5.<sup>84,85</sup> These values for  $\text{H}_2$  can be obtained directly from diagonalization of the full spectral-product Hamiltonian of Eq. (20), or from the unitary transformation of Eq. (33), with identical values resulting from the two procedures in the limit of closure. The total energies and binding energies and the expectation values of the electron transposition operator  $\hat{P}_{12}$  for both states shown in Table 2 evidently converge monotonically in both cases to known values<sup>86</sup> with increase in the angular momentum character of the atomic basis states employed. Similarly, the norms of the familiar singlet and triplet Heitler-London functions<sup>87</sup> represented in the spectral-product basis also shown in Table 2 give additional indication of the closure achieved for exchange terms in the wave functions this case. It is found in the finite basis sets of Table 1 that significantly more than one-half of the transformed Hamiltonian matrix of Eq. (33) is required in order to reproduce accurately the results obtained from the full spectral-product Hamiltonian matrix. That is, the symmetric and antisymmetric subspaces in this

case are not completely isolated by the unitary transformation of Eq. (33) into approximately one-half of the dimension of the original spectral-product basis, and the blocks of the Hamiltonian matrix of Eq. (60) identified as  $\{\mathbf{U}_S^\dagger(\mathbf{R}) \cdot \mathbf{H}(\mathbf{R}) \cdot \mathbf{U}_S(\mathbf{R})\}_{pp/uu}$  must include a sufficient number of small but non-zero “off-diagonal” contributions in order to achieve eigenvalues in accord with those obtained from the full Hamiltonian matrix. These results serve to emphasize that the development of Section 5 provides a formal proof of convergence of the atomic spectral method, rather than an optimal computational implementation of the approach, and that additional Gaussian or alternative basis functions and other computational strategies are required to improve the rate and degree of convergence achieved.

## 6.2 Recursive Construction of the Subspace Hamiltonian

The metric matrix and the corresponding explicit unitary transformation of the Hamiltonian of Section 5 are avoided employing a recursive method to generate sequences of (Krylov-Lanczos) basis states which span the two permutation-symmetry subspaces of the spectral-product basis of Eq. (70). The development employs symmetric or antisymmetric starting functions in its implementation, essentially constructing the subspace  $\Phi_S^{(p)}(\mathbf{1}; \mathbf{2} : R)$  of Eq. (55) contained in Eq. (70) around a chosen function of good symmetry, and avoiding the unwanted subspace  $\Phi_S^{(u)}(\mathbf{1}; \mathbf{2} : R)$  entirely. In this way, tri-diagonal Hamiltonian matrices of much lower dimensions than that of Eq. (70) can be constructed which converge to unitary equivalent representations of the totally symmetric or antisymmetric blocks of  $\mathbf{H}(R)$  without explicit evaluation and storage of the entire metric matrix or the Hamiltonian matrix required in Section 5.

Following largely standard procedures,<sup>80,81</sup> an orthonormal symmetric or antisymmetric Krylov-Lanczos  $[v_j(\mathbf{1}; \mathbf{2} : R), j = 1, 2, \dots, j_{max}]$  subspace of the spectral-product basis is written in the form

$$v_j(\mathbf{1}; \mathbf{2} : R) = \Phi(\mathbf{1}; \mathbf{2} : R) \cdot \mathbf{v}_j(R), j = 1, 2, \dots, j_{max}, \quad (72)$$

where the column vectors  $\mathbf{v}_j(R)$  are obtained from the recursive Lanczos equations<sup>80,81</sup>

$$\beta_j(R) \mathbf{v}_{j+1}(R) = [\mathbf{H}(R) - \alpha_j(R)\mathbf{I}] \cdot \mathbf{v}_j(R) - \beta_{j-1}(R) \mathbf{v}_{j-1}(R), j = 1, 2, \dots, j_{max}. \quad (73)$$

Here,  $\mathbf{v}_0(R)$  can be taken as a null vector without loss of generality and  $\mathbf{v}_1(R)$  obtained using Eq. (72) from a suitably chosen symmetric or antisymmetric starting function (see below). The coefficients  $\alpha_j(R)$  and  $\beta_j(R)$ , given by the expressions

$$\alpha_j(R) = \mathbf{v}_j(R)^\dagger \cdot \mathbf{H}(R) \cdot \mathbf{v}_j(R) \quad (74)$$

$$\beta_j(R) = \mathbf{v}_{j+1}(R)^\dagger \cdot \mathbf{H}(R) \cdot \mathbf{v}_j(R) \quad (75)$$

obtained directly from Eq. (73) and the imposed orthonormality of the  $\mathbf{v}_j(R)$ , provide the diagonal and off-diagonal elements of the symmetric or antisymmetric block of the Hamiltonian matrix in tri-diagonal form. A sequence of approximations to either of the subspace Hamiltonian matrices is obtained in this way with increasing order  $j_{max}$ , whereas convergence is achieved in the limit  $j_{max} \rightarrow \infty$ .<sup>70</sup>

To ensure that the sequence of basis states of Eqs. (72) to (75) generates a proper subspace of the spectral-product basis, and that the tri-diagonal Hamiltonian matrix of Eqs. (74) and (75) so constructed is unitarily equivalent to the symmetric or antisymmetric block of the spectral-product Hamiltonian matrix, the function required to start the recurrence of Eqs. (73) to (75) must be explicitly symmetric or antisymmetric and have nonzero projection on the entire spectral-product basis. These requirements ensure that all the states in the sequence of Eq. (72) will be explicitly symmetric or antisymmetric in the closure limit, consequent of the permutation-symmetric nature of the Hamiltonian in Eq. (73).

Once the Krylov-Lanczos sequence has been constructed employing Eqs. (72) to (75), corresponding Schrödinger eigenfunctions are obtained in the form<sup>70</sup>

$$\begin{aligned}\Psi_{\Gamma}(\mathbf{1}; \mathbf{2} : R) &= N_{\Gamma}(R) \sum_{j=1}^{j_{max}} q_j(E_{\Gamma}(R)) v_j(\mathbf{1}; \mathbf{2} : R) \\ &= N_{\Gamma}(R) \Phi(\mathbf{1}; \mathbf{2} : R) \cdot \sum_{j=1}^{j_{max}} q_j(E_{\Gamma}(R)) \mathbf{v}_j(R),\end{aligned}\quad (76)$$

where  $N_{\Gamma}(R) = \{\sum_{j=1}^{j_{max}} q_j(E_{\Gamma}(R))^2\}^{-1/2}$  is a normalization factor, the orthogonal polynomials  $q_j(E)$  satisfy the recurrence relation

$$\beta_j(R) q_{j+1}(E) = [E - \alpha_j(R)] q_j(E) - \beta_{j-1}(R) q_{j-1}(E), \quad j = 1, 2, \dots, j_{max}, \quad (77)$$

and the starting conditions for the recurrence are  $q_0(E) = 0$  and  $q_1(E) = 1$ . The associated energies  $E_{\Gamma}(R)$  are obtained from the secular equation  $q_{j_{max}+1}(E_{\Gamma}(R)) = 0$ , with the  $q_j(E)$  characteristic polynomials of the Hamiltonian in the Krylov-Lanczos basis.<sup>80,81</sup> The development of Eqs. (73) to (77) is identical to use of the unitary transformation of Eqs. (53) to (62) when  $j_{max}$  approaches the dimension of the spectral-product basis, but is much more rapidly convergent to specific portions of the subspace of physical solutions than is the approach described in Section 5. This is because appropriately chosen starting functions  $v_1(\mathbf{1}; \mathbf{2} : R)$  can act as points of spectral concentration about which optimal Hilbert space descriptions of the desired physical states are built by the iterations of Eqs. (73) to (75).<sup>70,80,81</sup>

In Figure 2 are shown  $^1\Sigma_g^+$  and  $^3\Sigma_u^+$  potential energy curves in  $\text{H}_2$  obtained from the recursive development of Eqs. (72) to (77) and the basis of Table 1 employing symmetric and antisymmetric Heitler-London test functions  $[v_1(\mathbf{1}; \mathbf{2} : R)]$  to construct the starting vector  $\mathbf{v}_1(R)$  in each case. These reference states are excellent zeroth-order approximations to the physical states desired, with the leading tri-diagonal Hamiltonian matrix element ( $\alpha_1$ ) the Heitler-London energy in each case. As the iteration of Eqs. (73) to (75) proceeds, the relatively low-order tri-diagonal matrices obtained provide rapidly converging approximations to the desired subspace energy and wave function corresponding to the chosen starting function, avoiding explicit diagonalizations of large-dimensioned Hamiltonian or matrix matrices. Evidently, the potential curves of Figure 2 obtained converge rapidly in the chemical region ( $R = 1$  to  $5 a_0$ ) with increase in the orbital angular momentum values

employed, the  $[sp]$  limit already providing  $\approx 90\%$  of the chemical bonding energy at the equilibrium interatomic separation, and the higher values providing results in increasingly good agreement with the correct values. The Heitler-London functions for  $H_2$  are well represented in the spectral-product basis [Eq. (72)] at the equilibrium internuclear separation [see Table 2], but must be included explicitly as supplements to the basis at larger separation in Figure 2, rather than employing the expansion of Eq. (72). In this latter event, one additional row and column is added to the matrix  $\mathbf{H}(R)$  in Eq. (73), although the development of Eqs. (72) to (77) is otherwise unchanged.<sup>84</sup>

Finally, although the present implementation of the development was not devised specifically to study the van der Waals region of bonding, it is satisfying that the correct long-range energy limit is nevertheless obtained automatically from the recursive projection procedure. In Figure 3 are shown energy curves obtained from the present development in the long-range region ( $R \geq 12 a_0$ ), in which interval the singlet and triplet energies are indistinguishable, in comparison with values calculated employing standard singles and doubles configuration-interaction methods in the indicated basis sets. These results are plotted in a manner [ $R^6\{E(R \rightarrow \infty) - E(R)\}$  vs  $1/R^2$ ] that allows extraction of the two leading van der Waals coefficients. The  $C_6$  coefficients ( $\approx 6.45 au$ ) obtained from the  $(1/R^2) \rightarrow 0$  limits of both sets of calculations in the  $[6s6p]$  basis set are evidently in mutual agreement and also in general accord with the known correct value ( $6.499 au$ ).<sup>89</sup> Similarly, the  $C_8$  coefficients ( $\approx 123 au$ ) obtained from the slopes of the curves in Figure 3 calculated in the  $[6s6p6d]$  basis set are also in accord with the known value ( $124.4 au$ ).<sup>90</sup> By contrast, although the energy curves obtained from the atomic spectral development follow the conventional singles and doubles configuration-interaction calculations for larger  $R$  ( $\geq 15 a_0$ ) values, they do not reproduce the curvatures in the configuration-interaction results for smaller  $R$  values. This circumstance is a consequence of the need for larger or alternative basis sets, and possibly higher angular momentum terms [see Table 2], required by the spectral method to insure convergence, which terms are absent in the results of Figure 3. That is, the energy curve in the  $12 \leq R \leq 15 a_0$  region is not accurately represented by the asymptotically correct Heitler-London term and the  $[6s6p]$  and  $[6s6p6d]$  spectral-product basis sets employed in Figure 3, emphasizing the well-known sensitivity of the small interaction energies in the long-range region to the effects of electron exchange.<sup>28,86</sup>

## 7. Discussion and Concluding Remarks.

The atomic spectral method described here adopts a new perspective on calculations of the electronic structures of molecules and other atomic aggregates. Enforcement of wave function antisymmetry in an atomic spectral-product basis is deferred until after construction of the Hamiltonian matrix, the latter consequently taking a particularly simple form which involves only unperturbed atomic energies and pairwise-atomic (Coulombic) interactions. The required interaction energies are obtained from atomic transition-density matrices which can be calculated once and for all, providing thereby a quantitative approach to the quantum theory of matter in terms of spectral attributes of its atomic constituents. Antisymmetry requirements are subsequently enforced employing a unitary transformation implemented by recursive methods devised specifically for this purpose. These and related aspects of the method are illustrated with calculations on molecular hydrogen ( $H_2$ ), which demonstrate convergence to results obtained from conventional prior

antisymmetrization methods. Additional applications of the formalism presently underway should help to demonstrate the viability of the development in cases in which non-Pauli representations are present.

The theoretical development adopts the methodologies and attributes of a variety of conventional methods for determining the adiabatic electronic wave functions and energies of chemical aggregates. Use of the atomic spectral-product basis dates from early perturbation-theoretical treatments of atomic interactions<sup>25</sup> and related later efforts to incorporate the effects of electron exchange in this context.<sup>26–38</sup> In contrast to these approaches, the present development is non-perturbative in nature and is applicable to both chemical and physical (noncovalent) interatomic interactions on a common basis. Although explicit electron exchange is avoided at the outset, the totally antisymmetric subspace of the atomic spectral-product basis is isolated and the unphysical non-Pauli representations are avoided.<sup>26–38</sup> Convergence is ensured in this way to the physically significant eigenstates contained in the spectral-product representation, providing non-perturbative methods for avoiding the non-Pauli states that accompany the change in symmetric group consequent of aggregate formation.<sup>32,37</sup> Although convergence is ensured in the limit of closure, it remains to illustrate in greater detail the computational efficiency of the method described for recursive isolation of the physical subspace in more complex cases in which large numbers of unphysical discrete and continuum states are present. Additionally, although no explicit mention is made here of perturbative solutions in the totally antisymmetric subspace, this option has been previously considered and remains to be explored in complete detail.<sup>45</sup> Of particular interest in this connection is the efficient incorporation of charge-transfer and other explicitly antisymmetric terms in the form of chemically significant reference functions to accelerate convergence of the development to antisymmetric states, and to ensure that the correct numbers of degenerate multiplets are obtained in long-range interaction limits.

An explicitly antisymmetrized atomic spectral-product basis has been employed previously in so-called atoms-in-molecules approaches,<sup>46–50</sup> dating from early observations of the inadequacy of atomic-orbital representations in describing atomic multiplet orderings and of their consequent unsuitability for calculations of total molecular energies.<sup>46</sup> The present development generalizes the notions of this approach in a rigorous manner employing the atomic charge and transition densities of the non-interacting atomic constituents. As a consequence of Brillouin’s Theorem,<sup>63</sup> such one-electron properties are commonly understood to be less sensitive to the effects of electron correlation than are total molecular energies. Once the atomic charge- and transition-density matrices are determined employing conventional atomic-structure methods, they can be employed repeatedly in calculations of the required (Coulombic) atomic interactions. The incorporation of experimental atomic energies in the Hamiltonian matrix, if required, is straightforward, and the form of the matrix obtained is considerably simpler than in the original atoms-in-molecules approaches.<sup>46–50</sup> Most important, the convergence of the present method is assured in the spectral closure limit, and difficulties associated with potential linear-dependence are avoided entirely in the orthonormal representation employed. In light of these attributes, largely consequent of separation of Hamiltonian matrix construction from the enforcement of wave function antisymmetry, the present development provides an atoms-in-molecules



strategy alternative to that devised many years ago and employed in various forms in the interim. Although no explicit mention is made here of incorporating diatomic calculations or other related information in aggregate studies,<sup>51–58</sup> this approach has been described previously and employed in computational applications to the structures, spectra, and dissociation dynamics of atomic clusters.<sup>45,91</sup> The important theorems upon which these studies are based and a more detailed accounting of this variant of the atomic spectral development are subjects of separate reports.

The relatively simple forms of the two-center interaction terms required in constructing the atomic spectral-product Hamiltonian matrix allows its representation in a wider range of orbital functions than the Gaussians commonly employed in conventional electronic structure calculations. In particular, Slater forms allow for efficient evaluations of the required interaction integrals,<sup>71,72</sup> potentially providing better representations of the atomic states and associated one-electron transition densities required in the development than those obtained in Gaussian representations. The *ab initio* methods currently in use for constructing the ground and excited electronic states of atoms and molecules can be adopted for this purpose with little modification.<sup>7–12</sup> Although these methods as currently employed can provide highly accurate results for atomic systems, they require allocations of significant computational resources in order to perform the repeated electronic structure calculations at different molecular geometries required in constructing potential energy surfaces and related properties of molecules. Additionally, they generally deal with total electronic energies, rather than with atomic binding energies, in spite of the well-known difficulties inherent in such approaches, the constituent atoms making their presence apparent only through the commonality of atomic basis sets employed in such calculations.<sup>39–44</sup> By contrast, the present approach avoids repeated high-level molecular calculations of total aggregate energies and adopts the *ab initio* methods only in accurate calculations of atomic spectral states and their one-electron transition densities. Use of the orthonormal spectral-product basis also circumvents the well-known basis-set superposition difficulties associated with conventional approaches,<sup>92</sup> which have proved particularly troublesome in studies of non-covalent interactions. Of course, systematic methods must be devised for construction and tabulation of the atomic information required for implementation of the present approach, in which connection it should be noted that atomic spectra are of considerable interest in their own right,<sup>93</sup> separate from their use in the context of calculations of aggregate electronic structures.

The widely employed density-functional-theory (DFT) approaches provide useful structural and other ground-state information for large molecules and atomic aggregates,<sup>13–17</sup> and can be extended to studies of dynamical response functions for calculations of excited-state properties.<sup>18</sup> Although the present approach is based on largely pedestrian theoretical concepts, and entails no approximations other than those of a computational nature, it nevertheless has some theoretical commonality with the DFT methods in the shared attempt to circumvent complexities associated with antisymmetry requirements, although by different means. Specifically, conventional antisymmetric methods are employed in calculations of the required atomic spectral information, but the Coulombic atomic interaction potentials employed in the present approach to aggregate formation are constructed in the absence of inter-atomic exchange effects, and are, therefore, largely unphysical. Relatedly,

attempts to incorporate explicitly the subtle effects of electron correlation in the DFT approaches to van der Waals interactions apparently<sup>94</sup> lead naturally to the one-electron transition-density matrices of particular computational focus in the present development, suggesting that study of possible adoption of DFT methods in the present context may be beneficial.

Finally, although it is premature to discuss the possible role of the present development in connection with semi-empirical and QM/MM approaches to larger systems,<sup>19–24</sup> there may ultimately be some relevance in this connection in view of the atomic-interaction perspective adopted, and in light of the growing importance of such methods to studies of proteins and other biological macromolecules.<sup>24</sup> Particularly needed are higher-level QM methods to treat proton and electron transfer, and the isomerizations and other motions of optical chromophores, in the presence of solvating protein or other environments. Additionally, it would be highly desirable to develop methods that can avoid the QM-MM boundary effects experienced in some applications of current methods, among the other challenges such studies present.

The foregoing issues and additional matters associated with more general implementations of the atomic spectral approach clearly require studies well beyond the scope of the present report. Investigations of these matters and the results of computational applications to other systems currently in progress will be described in due course.

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**Table 1. Spectral Energies for Atomic Hydrogen.<sup>a</sup>**

s-basis <sup>b</sup>	p-basis <sup>b</sup>	d-basis <sup>b</sup>	f-basis <sup>b</sup>
−0.499991	−0.124998	−0.055256	−0.026707
−0.124994	−0.053439	−0.011199	0.028807
−0.048465	0.025060	0.108901	0.187597
0.088668	0.274825	0.450236	0.617389
0.563368	0.986192	1.361055	1.748440
1.951139	2.880038	3.708833	4.791877
5.660465	7.854649	9.719458	
15.152536	21.314359	25.786063	
38.982050			
98.333482			
249.224098			
657.488778			

<sup>a</sup> Orbital energies (*au*) obtained from diagonalization of the atomic hydrogen Hamiltonian employing the indicated basis sets.<sup>82–85</sup>

<sup>b</sup> Basis sets employed are the most diffuse [12s8p8d6f] primitives chosen from a set of 14 even-tempered Gaussian primitives for each angular momentum symmetry, which set consists of 12 regularized even-tempered primitives<sup>82</sup> supplemented with two additional primitives in each symmetry having exponents of 0.02786 and 0.01156.



**Table 2. Electron Pair-Bond Calculations.<sup>a</sup>**

Basis <sup>b</sup>	Energy(a.u.) <sup>c</sup>	Binding(eV) <sup>c</sup>	$\langle \hat{P}_{12} \rangle^c$	$( \Phi^{(HL)} ^2)^c$
<sup>1</sup> $\Sigma_g^+$ state				
[s]	-1.0096	+0.2618	+0.5255	+0.8052
[sp]	-1.0691	+1.8809	+0.8409	+0.9469
[spd]	-1.1140	+3.1027	+0.9525	+0.9872
[spdf]	-1.1384	+3.7667	+0.9847	+0.9967
Exact <sup>86</sup>	-1.1745	+4.7478	+1.0000	+1.0000
<sup>3</sup> $\Sigma_u^+$ state				
[s]	-0.5586	-12.0109	-0.6226	+0.2950
[sp]	-0.6641	-9.1400	-0.6905	+0.8078
[spd]	-0.7249	-7.4856	-0.9317	+0.9538
[spdf]	-0.7524	-6.7372	-0.9801	+0.9870
Exact <sup>86</sup>	-0.7842	-5.8737	-1.0000	+1.0000

<sup>a</sup> Values at  $R = 1.40 a_0$  obtained from diagonalization of the Hamiltonian matrix of Eqs. (20) to (25) for H<sub>2</sub>, or, equivalently, from the unitary transformation of Eq. (33) in the text.<sup>84,85</sup>

<sup>b</sup> Denotes the portion of the [12s8p8d6f] basis set indicated in Table 1 employed in the calculation.

<sup>c</sup> Total and binding energies as indicated;  $\langle \hat{P}_{12} \rangle$  refers to the expectation value of the electron transposition operator  $\hat{P}_{12}$ ;  $|\Phi^{(HL)}|^2$  is the norm of the Heitler-London function as represented in the spectral-product basis.

## Captions for Figures

Figure 1. Eigenvalues  $s_i$  of the metric matrix of Eqs. (39) and (71) for  $H_2$ , constructed in the  $[12s8p]$  basis set of Table 1 as functions of interatomic separation  $R(a_0)$ .<sup>84,85</sup> values  $s_i \approx 2$  refer to approximately antisymmetric eigenfunctions of electron coordinates constructed in the spectral-product basis, whereas values  $s_i \approx 0$  refer to approximately symmetric functions of electron coordinates, as is discussed more fully in the text; apparent discontinuities in the slopes of the plots are due to the coarse grid in  $R$  values employed.

Figure 2. Total energy ( $au$ ) curves for the  $^1\Sigma_g^+$  and  $^3\Sigma_u^+$  states of  $H_2$  as functions of atomic separation  $R(a_0)$ : heavy solid lines refer to previously determined accurate values;<sup>86</sup> light solid lines refer to Heitler-London values;<sup>87</sup> dashed lines give the present results obtained from the recursion procedure indicated in the text employing the  $[s]$ ,  $[sp]$ , and  $[spd]$  basis states of Table 1 and Heitler-London test functions in each case.<sup>83,84</sup>

Figure 3. Potential energy ( $au$ ) curves for the  $^1\Sigma_g^+$  state of molecular hydrogen in the long-range interaction region obtained as indicated: open squares - accurate values obtained from single and doubles configuration-interaction calculations in  $[6s6p]$  and  $[6s6p6d]$  basis sets consisting of six regularized even-tempered primitive Gaussian orbitals of each angular momentum symmetry;<sup>82</sup> solid circles - spectral theory results obtained from the recursive development of Eqs. (73) to (77), calculated employing the indicated basis sets; lines - fits to the straight-line portions of the calculated values; the  $(1/R^2) \rightarrow 0$  intercept gives  $C_6 = 6.45 au$ , whereas the slope of the  $[6s6p6d]$  curve in this limit gives  $C_8 = 123 au$ , in good accord with the known values of 6.499 and 124.4  $au$ , respectively.<sup>89,90</sup>

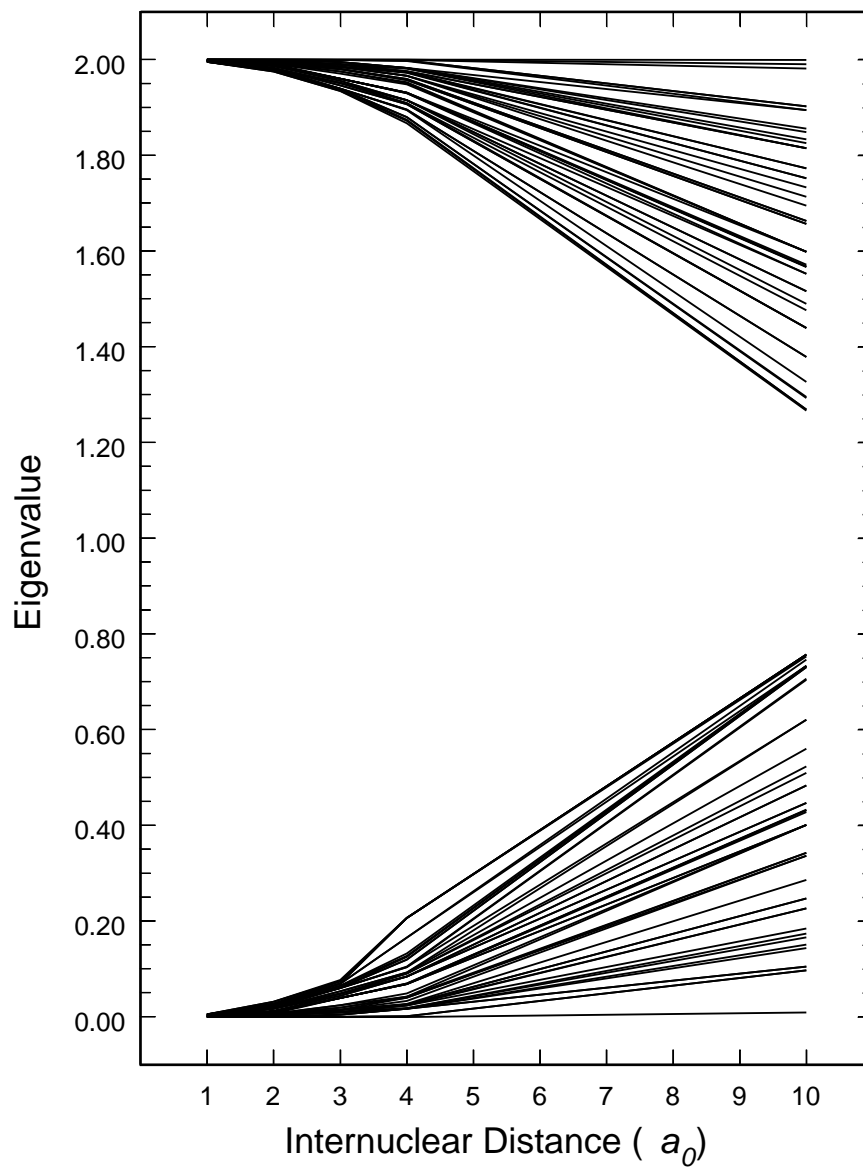


Figure 1—Langhoff et al, Journal of Chemical Physics

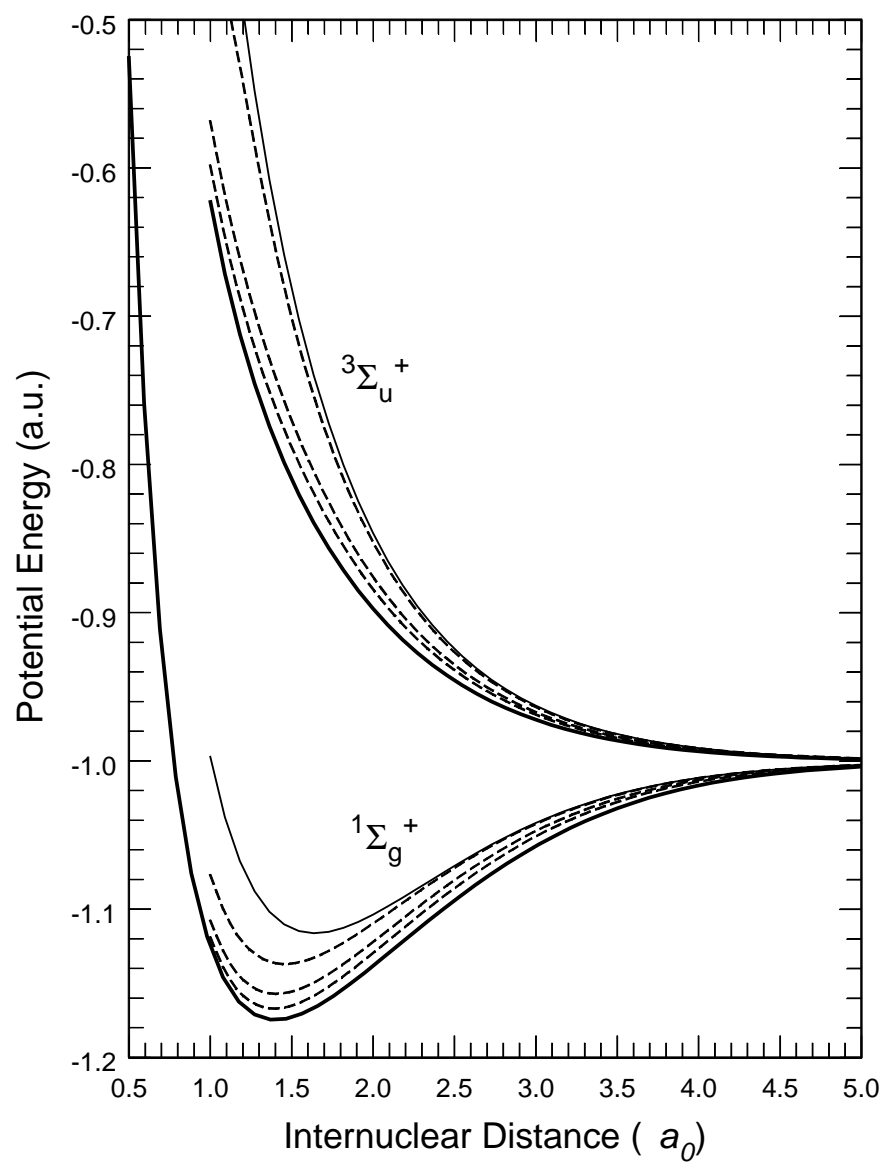


Figure 2—Langhoff et al, Journal of Chemical Physics

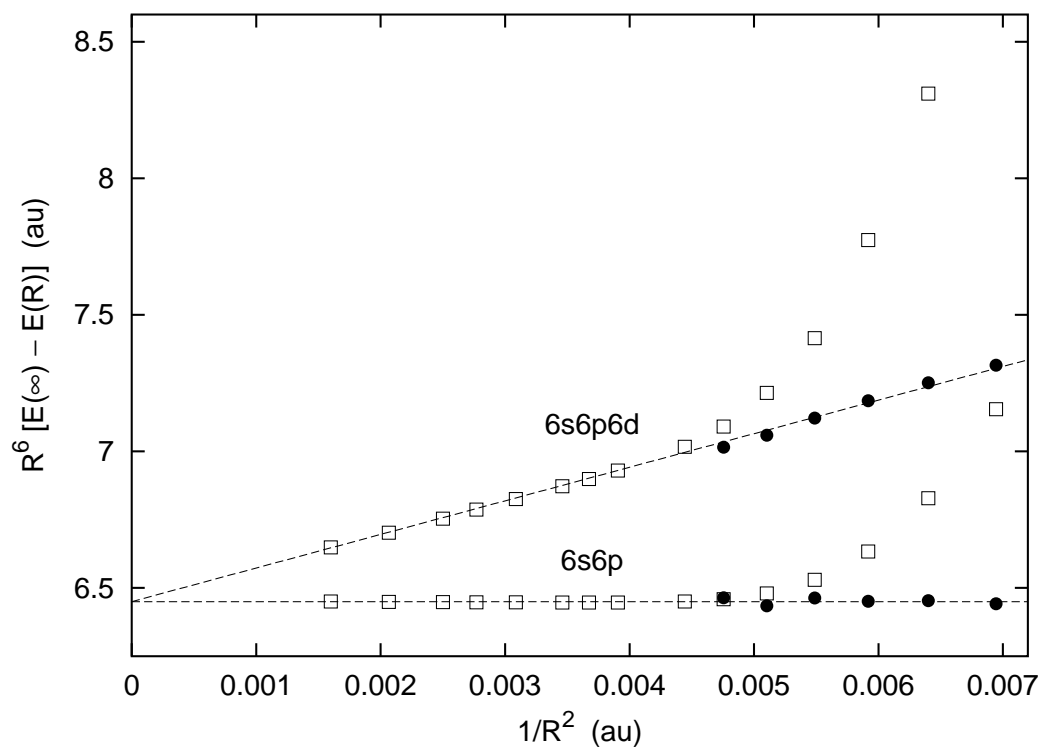


Figure 3—Langhoff et al, Journal of Chemical Physics